Lake Washington Watershed PCB and PBDE Loadings Field Study

Quality Assurance Project Plan

Part of the Study: Modeling PCB/PBDE Loadings Reduction Scenarios for the Lake Washington Watershed

March 2011

FINAL

King County

Department of Natural Resources and Parks
Water and Land Resources Division
Science and Technical Support Section
King Street Center, KSC-NR-0600
201 South Jackson Street, Suite 600
Seattle, WA 98104
206-296-6519 TTY Relay: 711
www.kingcounty.gov/environment/wlr/science-section.aspx

Alternate Formats Available

206-296-7380 TTY Relay: 711

Lake Washington Watershed PCB and PBDE Loadings Field Study

Quality Assurance Project Plan

Prepared by:

King County Department of Natural Resources and Parks
Water and Land Resources Division
Seattle, WA 98104

King County
Department of Natural Resources and Parks
Water and Land Resources Division
Science and Technical Support Section

Prepared for United States Environmental Protection Agency and King County Department of Natural Resources and Parks

Jenée Colton, King County, Project Manager

Randy Shuman, King County, Science Manager

Richard Jack, King County, Project QA Officer

Gina Grepo-Grove, EPA Region 10, QA Manager

Michael Cox, EPA Region 10, Technical Officer

Melissa Whitaker, EPA Region 10, Project Officer

Disclaimer:

This project has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement PC-00J285-01 to King County. The contents of this document do not necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

THIS PAGE INTENTIONALLY LEFT BLANK

Table of Contents

Abstract viii
1.0. Introduction 1
1.1 Study Need 1
1.2 Study Area 2
1.3 Historical Data Review 5
1.3.1 Ambient Water Data 5
1.3.2 Stormwater Data 5
1.3.3 Combined Sewer Overflow Data 6
1.3.4 Highway Runoff Data 6
1.3.5 Air deposition Data 7
1.3.6 Ambient Sediment Data 7
1.3.7 Fish Tissue Data 11
1.3.8 YSI Lake Buoy Data 12
1.3.9 Existing Data Summary 12
2.0. Data Quality Objectives 13
2.1 Precision, Accuracy, and Bias 13
2.2 Representativeness 15
2.3 Completeness 16
2.4 Comparability 16
2.5 Sensitivity 16
3.0. Sampling Design 17
3.1 Site Selection 20
3.1.1 Ambient Sites 22
3.1.2 Stormwater and Highway Runoff 25
3.1.3 CSO 25
3.1.4 Atmospheric deposition 26
3.2 Sampling Methods 27
3.2.1 Ambient Lake Washington and Ship Canal waters 27
3.2.2 Cedar and Sammamish River Waters 27
3.2.3 Tributaries 28

3.2.4 Stormwater discharge pipes....28
3.2.5 Combined sewer pipes....29
3.2.6 Direct Road Runoff....29
3.2.7 Air Deposition....29
3.2.8 Sampling Station Locations and Sample Identification....30
3.2.9 Sample Acquisition and Analytical Parameters....30
4.0. Sampling Procedures....32
4.1 Sampler Decontamination and Sample Collection....32
4.1.1 Ambient Water Samples....32
4.1.2 Autosampling Combined Sewer Pipe, Stormwater Pipe, and Bridge Runoff Samples....32
4.1.3 Air Deposition Samples....33
4.2 Sample Delivery and Storage....34
4.3 Chain of Custody....35
4.4 Sample Documentation....35
4.5 Acceptance of Supplies and Consumables....36
4.6 Field Measurements....36
4.7 Field Instrument Testing, Inspection, Calibration and Maintenance Frequencies....37
4.8 Field Replicates....37
4.9 Field and Equipment Blanks....37
4.10 Bulk Deposition Field QC....38
4.10.1 Dry Deposition QC Samples....38
4.10.2 Wet Deposition QC Samples....44
5.0. Analytical Methods and Detection Limits....45
5.1 PCB Congeners in Waters and QC Wipe Samples (i.e. Solids)....46
5.2 PBDE Congeners in Waters and QC Wipe Samples (i.e. Solids)....53
5.3 Conventionals....54
5.4 Laboratory Instrument Testing, Inspection, Calibration and Maintenance Frequency....56
6.0. Special Training and Certification....57
7.0. Data Validation, Reporting and Record Keeping....58
7.1 Data Validation....58
7.2 Reporting....58

7.3 Record Keeping and Data Management 58
7.4 Assessments and Response Actions 59
8.0. Project Responsibilities 60
9.0. Project Schedule 61
10.0. Index to QAPP elements 62
11.0. References 63

Figures

Figure 1. Greater Lake Washington Watershed 4
Figure 2. PCB Aroclors detected results in King County stormwater samples, 2000-2010. Insufficient numbers of detections to calculate $10^{th}/90^{th}$ percentiles. 6
Figure 3. South Lake Washington Total PCB Aroclor Concentrations in 0-2 cm Surface Sediments. Units are ug/kg dry weight. (Era-Miller, et al. 2010) 8
Figure 4. Comparison of North and South Lake Washington PCB Sediment Cores. Figure shows results for up to 26 cm depth (Era-Miller, et al. 2010) 9
Figure 5. PCB Aroclors detected in surface sediments of Lake Washington (detection limits varied by sample from 0.83 to 170 µg/Kg dw). Data from King County monitoring database. 11
Figure 6. Lake Union and Ship Canal detected PCB Aroclor results (detection limits varied by sample) 11
Figure 7. Sampling locations. 19
Figure 8. Rain Gauges for Determination of Storm Conditions 23

Tables

Table 1. Lake Washington water concentrations of total PCBs and total PBDEs as backcalculated from SPMD measurements (Sandvik, 2010). Concentrations in pg/L. 5
Table 2. Daily atmospheric deposition fluxes of total PBDEs at the West Point air deposition station, Puget Sound. Total PBDE (ng/m2/d). 7
Table 3. Number of samples collected per fish species from Lake Washington, Seattle, Washington between October 2001 and April 2003. 12
Table 4. Expected precision of replicates by sample type 14
Table 5. Site Selection Criteria 21
Table 6. Tributary, Stormwater, CSO and I-90 Sampling Site Information 24

Table 7. Sampling Stations and Methods and Sample Count 31

Table 8. Sample Container, Preservation, Storage, and Hold Time Requirements 34

Table 9. Congener Concentrations in Target Spikes for Air Deposition Re-volatilization QC Samples 39

Table 10. Congener Concentrations in Target Spikes for Air Deposition Re-volatilization QC Samples 42

Table 11. Labeled Surrogates and Recovery Standards Used for EPA Method 1668A PCB Congener Analysis by IUPAC[1] congener number 46

Table 12. PCB Congener water detection limits and lower calibration limits by EPA method 1668A, AXYS Analytical Services method MLA 010. Values in pg/L (or pg/sample for air deposition) based on 1 L sample but will be prorated for actual sample size. 48

Table 13. Labeled Surrogates and Recovery Standards Used for EPA Method 1614 PBDE Congener Analysis 53

Table 14. PBDE Congener water sample detection limits and lower calibration limits by EPA method 1614A, AXYS Analytical Services method MLA 033. Values in pg/L (or pg/sample for air deposition). 54

Table 15. Conventionals Analytical Methods and Detection Limits in mg/L 55

Table 16. Conventionals QA/QC Frequency and Acceptance Criteria for Water Samples 55

Table 17. Field Study Project Schedule 61

Appendix A, Bulk deposition sampler design

Appendix B, KCEL Autosampler SOP

Appendix C, Chain of Custody form

Appendix D, KCEL Attended Hydrolab SOP

Appendix E, KCEL Sealogger CTD SOP

Appendix F, AXYS Analytical PCB analysis SOP

Appendix G, AXYS Analytical PBDE analysis SOP

Appendix H, KCEL TOC/DOC SOP

Appendix I, KCEL TSS SOP

Distribution List

The following individuals will receive a copy of the project QAPP and any revisions or addenda.

King County

Jenée Colton, Grant Project Manager (206-296-1970) jenee.colton@kingcounty.gov

Richard Jack (206-405-5151) richard.jack@kingcounty.gov

Curtis DeGasperi (206-684-1268) curtis.degasperi@kingcounty.gov

Deborah Lester (206-296-8325) deborah.lester@kingcounty.gov

Colin Elliott (206-684-2343) colin.elliott@kingcounty.gov

Benjamin Budka (206-684-2328) ben.budka@kingcounty.gov

Sally Abella (206-296-8382) sally.abella@kingcounty.gov

AXYS Analytical Services LTD

Devin Mitchell, Project Manager (250-655-5812) dmitchell@axys.com

Dale Hoover, QA Officer (240-655-5800) dhoover@axys.com

EPA Region 10

Gina Grepo-Grove (206-553-1632) grepo-grove.gina@epa.gov

Michael Cox (206-553-1597) Cox.Michael@epamail.epa.gov

Melissa Whitaker (206-553-2119) whitaker.melissa@epa.gov

Project Advisory Panel

Fred Bergdolt (360-570-6648) BergdoF@wsdot.wa.gov

Betsy Cooper (206-263-3728) betsy.cooper@kingcounty.gov

Jonathan Frodge (206-684-8479) jonathan.frodge@seattle.gov

Jenny Gaus (425-587-3850) JGaus@ci.kirkland.wa.us

Joan Hardy (360-236-3173) Joan.Hardy@doh.wa.gov

Rachel McCrea (425-649-7223) rmcc461@ecy.wa.gov

Doug Navetski (206-296-7723) doug.navetski@kingcounty.gov

Andy Rheaume (425-556-2741) ajrheaume@redmond.gov

Ron Straka (425-430-7248) rstraka@renton.wa.gov

Bruce Tiffany (206-263-3011) bruce.tiffany@kingcounty.gov

Heather Trim (206-382-7007 X172) heatrim@gmail.com

Patrick Yamashita (206-275-7722) Patrick.Yamashita@mercergov.org

ABSTRACT

This study is designed to measure polychlorinated biphenyls (PCB) and polybrominated diphenylethers (PBDE) concentrations in key import and aqueous export pathways for Lake Washington and the Ship Canal. Whole water samples will be collected from Lake Washington along with the following import pathways: stormwater, CSO conveyance systems, highway runoff, major rivers and tributaries, and bulk air (wet and dry) deposition. The following export pathways will also be evaluated: the Montlake Cut (export from Lake Washington) and Hiram Chittenden Locks (export from the Ship Canal and the watershed). Samples will be collected during each of four quarters during a year. Field replicates will be collected where feasible. All samples will be analyzed for PCB and PBDE congeners using low level detection methods. In addition, samples will be analyzed for dissolved and total organic carbon (DOC and TOC) and total suspended solids (TSS) to characterize the organic and inorganic fractions in water.

Water concentration data will be combined with measured or modeled flow rates to estimate loadings. Annual loadings of PCBs and PBDEs to both Lake Washington and to Puget Sound via the outlet of the lake through the Lake Washington Ship Canal and Hiram Chittenden Locks will be calculated. The methodology of PCB and PBDE loadings calculations will be presented in a separate report.

1.0. INTRODUCTION

King County was awarded a grant by the Environmental Protection Agency (EPA) to determine polychlorinated biphenyl (PCB) and polybrominated diphenylether (PBDE) loading to Lake Washington, identify priority pathways, and estimate the decrease in fish tissue concentrations from potential PCB loading reductions. This Quality Assurance Project Plan (QAPP) covers the field study component of the project which is intended to fill data gaps. One goal of the field study is to measure concentrations in key types of import pathways (rivers, streams, stormwater, combined sewer overflows, and air deposition) to Lake Washington and the Ship Canal. The second goal of the study is to measure the concentrations in export pathways leaving the Lake Washington through the Ship Canal to Puget Sound. Flow will be measured by existing flow gauges or installed flow meters where feasible. These data will enable the first known estimates of current total PCBs and PBDEs loadings to the lake and the relative contributions from each pathway type, as well as total loadings of these contaminants to Puget Sound from the Greater Lake Washington watershed. The details of PCB and PBDE loadings calculations will be presented in a separate report.

1.1 Study Need

PCB concentrations in Lake Washington fish exceed both the National Toxics Rule (NTR) levels and the 95th percentile for all fish collected statewide (Seiders and Deligeannis 2009). In 2003, the Washington Department of Health (WDOH) issued a fish consumption advisory for PCBs in Lake Washington which covers yellow perch, cutthroat trout, carp, and northern pikeminnow.

The bioaccumulation of both PCBs and PBDEs presents potential health risks to aquatic life, wildlife, and humans. PCBs are established toxins which are noted to cause various reproductive effects in fish, wildlife and humans (EPA, 2010). They were voluntarily phased-out of production in 1977 and use in the United States was banned in 1979 (44 FR 31514). The exact toxicity of PBDEs remains unclear, but they are implicated in tumors, and neurodevelopmental and thyroid disorders. PBDEs have been banned in the European Union (Siddiqi, et al. 2003) and some forms have also been banned in Washington State (RCW 70.76).

This project represents one of the first efforts to measure PBDEs in Lake Washington water. Demetrius Fletcher's (2010) thesis presents a limited amount of data for PBDEs in water and fish within the Cedar River, but the sampling and processing methods employed generate considerable uncertainty around the water and the fish tissue concentrations.

Fish consumption advisories are ecosystem indicators of substantial water and/or sediment quality impairment. In the Greater Lake Washington watershed, it is not clear where regulatory or management actions should focus to achieve sufficient pollutant loading reductions. Scientific and water quality management staff of shoreline jurisdictions identified the fish advisory among their top water quality concerns during a watershed scoping exercise for Total Daily Maximum Load-related planning (Sinang Lee, pers. comm.). This project will fill data gaps and develop modeling tools to answer three management questions:

1. Which types of import pathways are the highest priorities for PCB/PBDE load reduction?

2. Will potential loading reductions from these pathways reduce fish bioaccumulation, and contribute substantially towards lifting the fish consumption advisory on Lake Washington?
3. How long might it take the system to respond to these hypothetical loading reductions?

The Greater Lake Washington drainage, which connects to the main basin of Puget Sound via the Hiram Chittenden Locks, is estimated as the third highest contributor of PCB loading to Puget Sound (Pelletier, 2009). However, PCB loading estimates to Puget Sound were based on extrapolation from literature values–no water data have been collected and analyzed using appropriate analytical detection limits, either from Lake Washington or waters between it and Puget Sound, to more directly quantify PCB loading. The field study component to this project will fulfill multiple data needs, including:

- Low level analysis of ambient surface water concentrations in Lake Washington.
- Whole water data for key import pathways to Lake Washington and from the watershed to Puget Sound.

The objectives of the field study component are:

- To collect whole water samples from potential major input pathways into Lake Washington or the Ship Canal, as well as water exiting the Ship Canal to Puget Sound.
- To analyze the whole water samples for PCBs and PBDEs at low detection limits, using standard methods to produce data of appropriate quality for use in loadings calculations, fate and transport, and bioaccumulation models.
- To measure the fractions of PCBs and PBDEs partitioned between particulate and dissolved water fractions in a subset of whole water samples. Measurements of partitioning are needed to calibrate fate and transport models.
- Analyze total organic carbon, dissolved organic carbon, and total suspended solids in all whole water samples for use in loadings calculations, fate and transport, and bioaccumulation models.
- Collect samples where flow can be measured for use in loading calculations.

For the purposes of this QAPP, the term “pathway” means a major hydrologic transport route carrying PCBs and PBDEs into or out of Lake Washington or the Ship Canal. Pathway does not include biologically mediated bioaccumulation or bioturbation within Lake Washington or the Ship Canal.

1.2 Study Area

The study area encompasses the Greater Lake Washington watershed (Figure 1). The Puget Sound shoreline drainages are not part of the study area. The watershed encompasses about 692 mi^2 (1,792 km^2), from its mouth at the Hiram Chittenden Locks, including Lake Union and the Ship Canal, drainages to Lake Washington including the Cedar River, the Sammamish River, Swamp, North, Little Bear and Big Bear Creeks, and the drainages to Lake Sammamish including Issaquah Creek. The two major rivers in the study area are the Sammamish River, which connects Lake Sammamish to the north end of Lake Washington, and the Cedar River which drains into the south end of Lake Washington.

Major cities located within the study area include Seattle (pop. 563,000), Bellevue (pop. 109,000), Redmond (pop. 46,900), Renton (pop. 54,800), and Kirkland (pop. 45,500). Overall, the study area has a population over 1 million and, at the current rate of growth, has a predicted population of 1.7 million in 2020 (Kerwin, 2001). Over 40 percent of the watershed's population resides in Seattle. Extensive population growth is currently occurring on the Sammamish Plateau east of Lake Sammamish, and throughout the northern drainages.

The study area also includes relatively undeveloped locations, consisting of evergreen and deciduous forests, riparian shorelines, and wetlands. The amount of developed land varies greatly between subbasins, ranging from heavily urbanized to almost entirely undeveloped.

Figure 1. Greater Lake Washington Watershed

1.3 Historical Data Review

The Greater Lake Washington watershed has been the subject of numerous environmental assessments and ambient monitoring programs. King County currently has an extensive water quality monitoring program; however, some of the bioaccumulative toxics of greatest concern, such as PCBs and PBDEs, have not been routinely analyzed in ambient water or the pathways considered here. This is, in part, because the low level analyses (pg/L to ng/L) required to measure concentrations of these contaminants in water is expensive and analytical capacity has not been possible until recent years. This section summarizes the PCB and PBDE data that exist from Lake Washington and the Ship Canal water, sediment, and fish analyses. Most of these analyses are reported in µg/L or µg/Kg range which is between one thousand and one million times greater than current picogram to nanogram PCB and PBDE congener analytical capabilities. Review of unpublished historical data has been generally limited to the last ten years due to uncertainties with sampling locations, techniques, and methods for older data.

1.3.1 Ambient Water Data

King County has conducted water quality monitoring for the Aroclor forms of PCBs for many years. Unfortunately, detection limits for this analysis have been higher than the concentrations present, making them undetectable. Washington State Department of Ecology has conducted a limited amount of surface water sampling for PCBs and PBDEs in Lake Washington at the entrance to the Ship Canal at the Montlake Cut (Sandvik, 2010). This analysis was conducted using semi-permeable membrane devices (SPMDs) which are polyethylene bags filled with a synthetic lipid. They serve to bioconcentrate otherwise very low ambient levels of hydrophobic chemicals to concentrations suitable for analysis. The water concentration is then back-calculated from the measured values. Ecology's calculated water concentration results are shown below in Table 1.

Table 1. Lake Washington water concentrations of total PCBs and total PBDEs as backcalculated from SPMD measurements (Sandvik, 2010). Concentrations in pg/L.

Chemical	April-May 2007	August-September 2007
Sum dissolved PCBs	42	31
Sum total PCBs	160	120
Sum dissolved PBDEs	25	39
Sum total PBDEs	170	270

1.3.2 Stormwater Data

Water concentrations of PCBs have not been routinely analyzed in stormwaters draining to the Lake Washington watershed with sufficiently low detection limits. King County Environmental Laboratory (KCEL) does not have the analytical capability to measure PBDEs in water. Historical King County monitoring programs have occasionally detected PCB Aroclors in

stormwater (King County unpublished data). These samples were collected as part of other projects and not part of targeted source control work in the Lower Duwamish Superfund site or elsewhere. Results of these analyses are shown below in Figure 2.

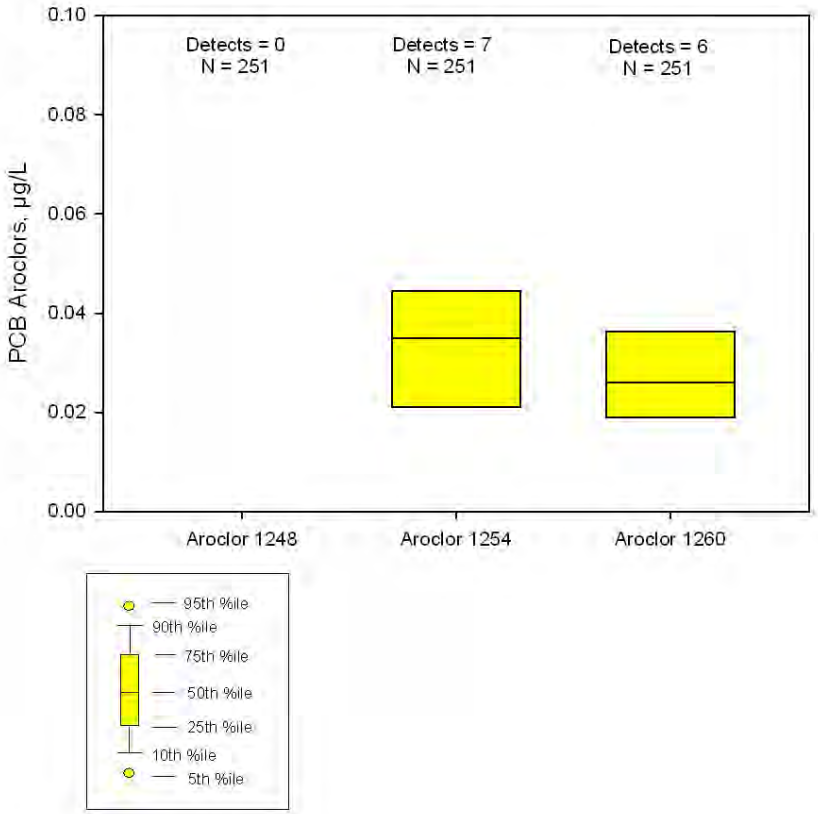


Figure 2. PCB Aroclors detected results in King County stormwater samples, 2000-2010. Insufficient numbers of detections to calculate $10^{th}/90^{th}$ percentiles.

These results include collaborative stormwater sampling with the City of Redmond in 2003 and 2006 which were all below the laboratory detection limit. Sample detection limits for 2000-2010 historic stormwater data varied between 0.0055 and 0.47µg/L.

1.3.3 Combined Sewer Overflow Data

No PCB or PBDE water data collected from combined sewer overflow pipes draining to Lake Washington or the Ship Canal could be located.

1.3.4 Highway Runoff Data

The 520 Bridge Stormwater Runoff Study (King County, 2005) analyzed runoff grab samples collected from the west high-rise of the SR-520 Floating Bridge. While many other semivolatile organic and metal contaminants were found, PCBs and PBDEs were not analyzed.

1.3.5 Air deposition Data

Brandenberger, et al. 2010 collected PCB and PBDE air deposition data at multiple locations around Puget Sound. The closest air deposition station to Lake Washington or the Ship Canal was located at the West Point wastewater treatment plant, which is approximately 2 km southwest of the Ship Canal and Hiram Chittenden Locks, the outflow point of the Lake Washington drainage to Puget Sound. PBDE deposition results are shown in Table 2.

Table 2. Daily atmospheric deposition fluxes of total PBDEs at the West Point air deposition station, Puget Sound. Total PBDE (ng/m2/d).

Station	Mean	Median	75th	25th	Min	Max
West Point, Seattle WA.	8.2	7.8	10.6	5.4	3.7	14.6

Nine field replicates were collected as part of this study (Brandenberger, et al. 2010) and relative percent differences (RPDs) were between 0 and 123%. When estimated data above the MRL but below the reporting limit were excluded, RPDs declined to 0-40%.

The Brandenberger et al. 2010 PCB data have not yet been reported. There are no other published studies of PCB deposition in the Puget Sound region. Literature reported PCB deposition rates in the United States vary between 0.04 $\mu g/m^2/yr$ and 16 $\mu g/m^2/yr$ (various as cited in EPA, 2007a and CBP, 1999).

1.3.6 Ambient Sediment Data

King County has conducted ambient sediment assessments of selected greater Lake Washington drainage water bodies like the Sammamish River (Colton, et al. 2005) and North Lake Washington Tributaries (Tetratech and Parametrix, 2003). PCBs were not detected above the method MRL in these sampling programs, while PBDEs were not analyzed.

Era-Miller et al. (2010) analyzed south Lake Washington 0-10 cm surface sediments and found mostly homogeneous concentrations of total Aroclors within the ranges found in unpublished 2000-2010 King County Lake Washington data. Figure 3 illustrates the spatial distribution of the Era-Miller et al. (2010) surface sediment data as well as their ranges.

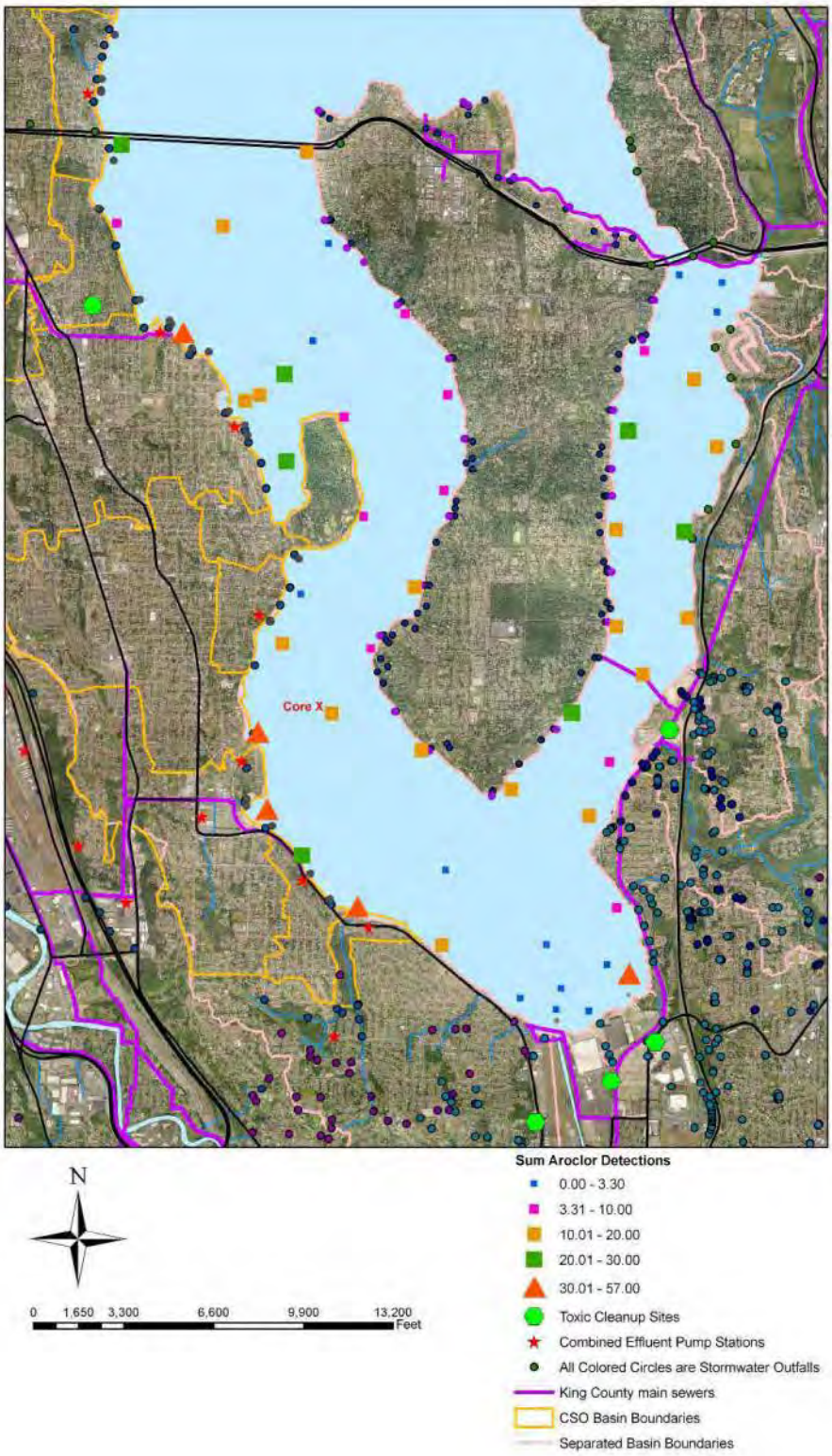


Figure 3. South Lake Washington Total PCB Aroclor Concentrations in 0-2 cm Surface Sediments. Units are ug/kg dry weight. (Era-Miller, et al. 2010)

Era-Miller's sediment study also collected a sediment core to evaluate PCB deposition over time. The study found that PCB concentrations in cores had declined from a peak in the late 1960s or early 1970s (Figure 4). Despite the decline, preliminary bioaccumulation estimates suggested that fish tissue concentrations were in equilibrium with the average surface sediment concentrations (Era-Miller, et al. 2010).

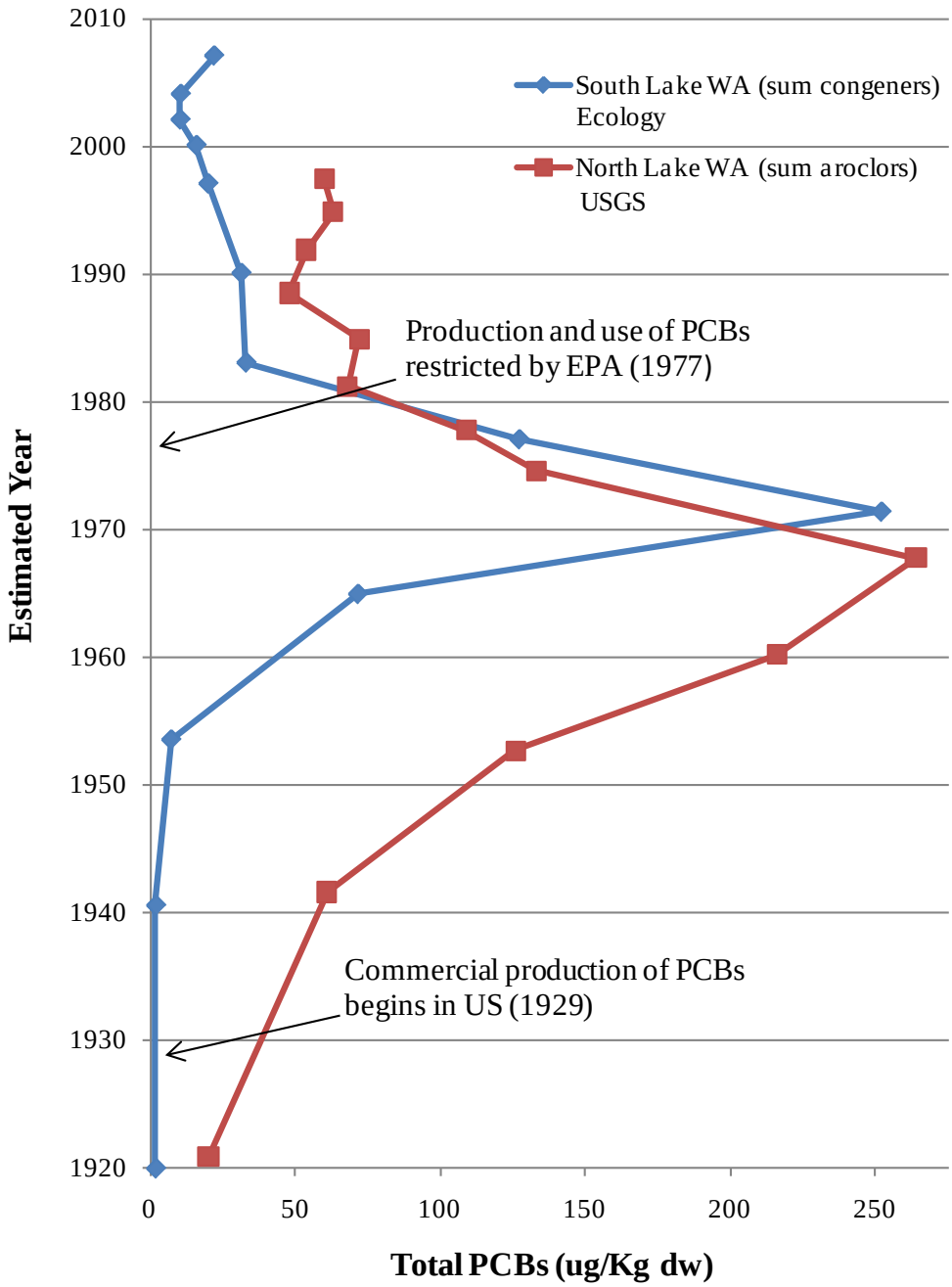


Figure 4. Comparison of North and South Lake Washington PCB Sediment Cores. Figure shows results for up to 26 cm depth (Era-Miller, et al. 2010)

King County sporadically monitored lake sediment for various projects in the past and also has an ambient sediment monitoring program which relies on rotating sampling stations to provide

spatial coverage over multiple years. This ambient sediment monitoring has not yet collected sufficient data to warrant spatial analysis or publication. However, unpublished King County ambient sediment monitoring data collected from 1999 to 2001 focused on monitoring possible impacts from various sources flowing into Lake Washington. Potential PCB sources include creeks and rivers, storm drains, combined stormwater overflows, and emergency sewer overflows. Results from the top 10 cm of sediment indicate that in general, sediment quality was good in the three lakes, however some PCB contamination was found in certain areas. There are no freshwater bioaccumulation based sediment quality guidelines available to describe the relative impact or magnitude of these PCB detections. However, the detections were typically found near stormwater outfalls and CSOs suggesting that these discharges continue to be potential factors affecting sediment quality. Major river and stream mouths generally had lower PCB sediment concentrations, illustrating that stormwater potentially impacts sediment quality.

Additional ambient sediment monitoring has occurred since the 1999-2001 PCB sediment study, but the results have not been published. To provide a more systematic review of sediment concentrations in the Greater Lake Washington watershed, all unpublished 2000-2010 King County sediment data were queried from King County's data management system (LIMS). These results revealed that Aroclors 1248, 1254, and 1260 were all detected in Lake Washington and Lake Union. Figures 5 and 6 illustrate these results. Moshenberg (2004) used a portion of these data to conduct a sediment quality triad analysis. She concluded that 70% of the major lakes sediment stations exceeded Canadian (Smith et al., 2002) and/or draft Ecology (2003) floating percentile sediment quality guidelines.

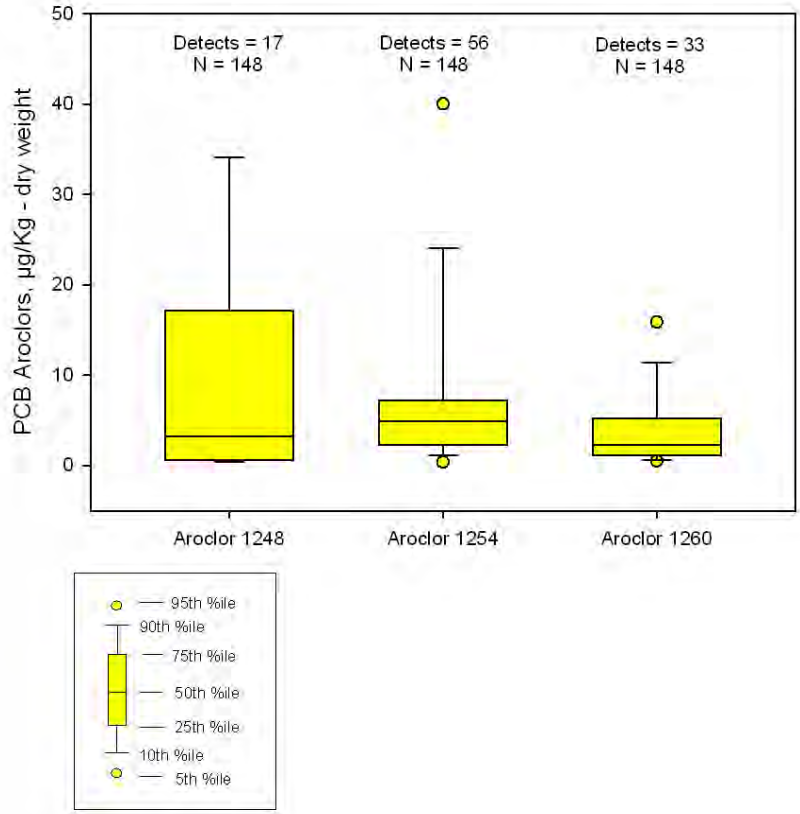


Figure 5. PCB Aroclors detected in surface sediments of Lake Washington (detection limits varied by sample from 0.83 to 170 µg/Kg dw). Data from King County monitoring database.

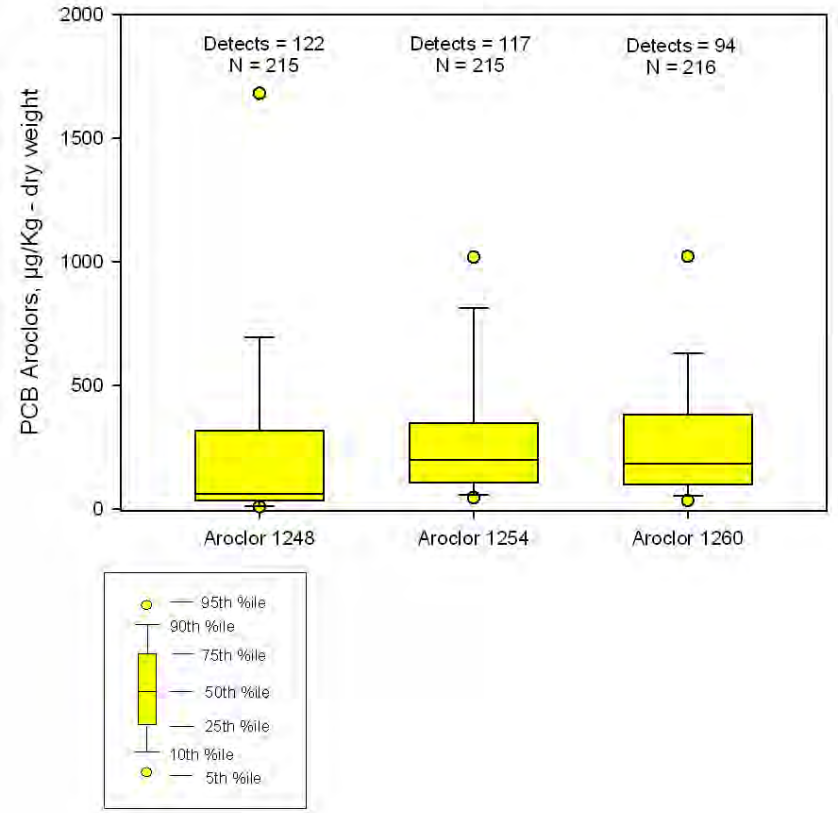


Figure 6. Lake Union and Ship Canal detected PCB Aroclor results (detection limits varied by sample)

Additional sediment sampling has not been proposed in this QAPP because sediments are not an external source of PCBs or PBDEs to Lake Washington or the Lake Union/Ship Canal. As Figure 6 illustrates, sediments are an eventual sink for contaminants like PCBs and PBDEs. This study's primary objectives (Section 2) are to better understand current inputs.

1.3.7 Fish Tissue Data

The majority of historical fish tissue data were collected by the University of Washington in cooperation with King County from 2001-2003 in Lake Washington. These data were subsequently provided to Washington Department of Health and form the basis of the current fish consumption advisory (DOH, 2004). These data are summarized in Table 3.

Table 3. Number of samples collected per fish species from Lake Washington, Seattle, Washington between October 2001 and April 2003.

Species	Sample Size	Size class	Mean PCB concentration (ppb)
Smallmouth Bass	3	All	371.2
Cutthroat Trout	10 10	<300mm >300mm	79.2 377.4
Yellow Perch	10 10 9	<200mm 201-271mm >271mm	46.6 66.4 191.1
Northern Pikeminnow	10 10	<300mm >300mm	140.0 1071.4
Sockeye Salmon	10	all	7.8

Additional fish tissue samples have been collected from Lake Washington by King County in 2010, but chemical analyses, including for PCB Aroclors and PBDEs, are not yet complete (King County, 2010).

1.3.8 YSI Lake Buoy Data

King County has installed and maintains a real time profiling buoy in Lake Washington. This buoy will be used to determine lake stratification and the depth of the epilimnion. Buoy specifications, QA limits, and real-time data are available on the internet (King County, 2011).

1.3.9 Existing Data Summary

PCBs have been sporadically analyzed and detected in a variety of media in the Greater Lake Washington drainage basin. In many cases older Aroclor-based analytical methods for water have low frequencies of detection coupled with higher method detection limits. Due to this, these data are of limited utility compared to modern congener methods for fate and transport, and bioaccumulation modeling. Where low detection limit methods have been applied, frequencies of detection have been high for PCBs and PBDEs in many media.

Methods for PBDE analysis were developed later than PCBs. Interest in PBDE measurement has been relatively recent (mid-2000s) and few data have been collected for sediment and fish tissue PBDE concentrations in Lake Washington.

2.0. DATA QUALITY OBJECTIVES

The data quality objectives (DQOs) are to collect data of known and sufficient quality to meet the project goals. Validation of project data will assess whether the data collected are of sufficient quality to meet the project goals. The data quality issues of precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity are described in the following sections.

2.1 Precision, Accuracy, and Bias

Precision is the agreement of a set of results among themselves and is a measure of the ability to reproduce a result. Accuracy is an estimate of the difference between the true value and the measured value. The accuracy of a result is affected by both systematic and random errors. Bias is a measure of the difference, due to a systematic factor, between an analytical result and the true value of an analyte. Precision, accuracy, and bias for analytical chemistry may be measured by one or more of the following quality control (QC) procedures:

- analysis of various laboratory QC samples such as blanks, surrogates, and replicates; and
- collection and analysis of field replicate and/or duplicate samples.

Because contaminant concentrations in some of the targeted pathways are known to be highly variable (e.g., stormwater) while others are thought to be relatively consistent (e.g. rivers), on average, precision is expected to be relatively low. Numbers and precision of field replicates for sampled matrices is expected to be within the ranges shown in Table 4. Professional judgment was used to predict precision because many of these pathways have not been sampled and analyzed by high resolution PCB/PBDE methods before in the Lake Washington area.

Table 4. Expected precision of replicates by sample type

Sample Type	Number of field replicates	Total PCB precision (RSD)	Total PBDE precision (RSD)	TOC, DOC, and TSS (RSD)
Lake Washington and Ship Canal ambient water	4 in Lake and 3 in Ship Canal	±20%	±40%	±20%
Lake Washington/H. Chittenden Locks outflow water	3	±25%	±40%	±20%
Cedar and Sammamish River water	3 in each river	±25%	±40%	±20%
Stormwater discharge outfalls	Up to 12	±50%	±50%	±20%
Tributaries	12 across all tributaries	±50%	±50%	±20%
CSO near-full pipe discharge	True replication not feasible			
Direct road runoff	4	±50%	±50%	±20%
Atmospheric deposition	At least 3 with 4 more archived	±50%	±50%	±20%

If precision does not meet the expected precision in Table 4, precision error will be incorporated into loadings estimates and used to guide future sampling efforts.

Accuracy, for PCB congener data is not directly quantifiable since certified reference materials do not exist for the suitable concentration ranges anticipated in water. Although the ongoing precision and recovery sample control charts used by the analytical laboratory provide some indication of overall accuracy. Additionally, the isotopic dilution methods chosen for this study is the most rigorous method for PCB and PBDE congener analysis. This method uses isotopically-labeled PCBs or PBDEs, respectively, to track the recovery performance of the range of congener homologs. Thus, each congener concentration is theoretically adjusted for the extraction efficiency and analytical performance of that specific sample.

Since this study intends to represent ambient conditions and storm/variable discharges, and these conditions vary in both time and space, sampling and analytical bias from actual conditions cannot be quantified.

2.2 Representativeness

Representativeness expresses the degree to which sample data represent a population, parameter variations at the sampling point, or an environmental condition.

Composite samples will be collected where possible to best obtain data representing average conditions. Where ambient waterbodies are deep enough and site access allows, samples will be collected at multiple depths for a composite sample. In locations where waterbodies are shallow and/or site access does not allow a composite sampler, grab samples will be collected. Given the large volume of water needed per sample, multiple grabs will be composited from a sampling event into one sample. Water samples in Lake Washington will be collected from multiple depths and separate samples will be collected above and below the thermocline during lake stratification. The thermocline is suspected to be a potential barrier to particulates passing into the hypolimnion when the lake is temperature-stratified (Shapiro, 1960). Measuring concentrations in separate samples from the epi- and hypolimnion will allow for testing of differences. Water samples at the Hiram Chittenden Locks will be composited across the water column to represent of PCBs and PBDEs exported to Puget Sound.

A range of storm intensities and subbasins will be sampled at locations where water levels are sensitive to storm conditions, i.e., stormwater conveyance and tributary locations. Where baseflow is present in these stormwater pipes, baseflow will be sampled. Where baseflow is not present, an additional storm will be sampled. This spatial and temporal distribution of stormwater pipe samples is intended to characterize the average annual contribution of these sources. The tributaries and the Sammamish and Cedar Rivers are assumed to be well mixed. Both wet and dry (baseflow) conditions will be targeted to evaluate annual averages.

CSO and stormwater sample collection will be targeted as close to the point of discharge as possible. Samples will be collected below any treatment technologies, which could remove solids, to obtain samples that best reflect both the dissolved and particulate fractions entering Lake Washington or the Ship Canal.

Direct road runoff will be measured from a downspout below the bridge deck on the I-90 Bridge, just before runoff falls into the lake. These samples are assumed to closely represent highway runoff that enters Lake Washington and the Ship Canal from I-90, SR-520, and I-5.

Atmospheric deposition samples are intended to represent the average wet and dry deposition to Lake Washington. One bulk deposition sampler will be deployed near the Lake Washington shoreline while the other bulk deposition sampler will be deployed at a long term Puget Sound ambient air monitoring station at Beacon Hill to evaluate differences between the immediate lakeshore and estimates of regional bulk deposition averages. The air deposition pathway, is relevant to understanding the stormwater pathways, as stormwater is a conveyor of pollutants from impervious surfaces.

The sample frequencies selected are anticipated to be most representative for well-mixed and large waterbodies in which flow changes over the timescale of months are <50%, i.e., major rivers, Lake Washington, Ship Canal, major tributaries. Sample representativeness decreases for sample types, such as stormwater and CSO discharges, for which flow changes are large and rapid. Because collection of these types of samples at any one location is limited by weather and sampling logistics, and PCB and PBDE loadings likely vary over space, stormwater stations will be distributed across multiple cities and collected during four consecutive quarters of a year.

2.3 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable analytical data are generated, compared to the total number of samples submitted for analysis. Sampling with adherence to standardized sampling and testing protocols will aid in providing a complete set of data for this study. The goal for completeness is 100% for ambient water and air deposition samples. The goal for completeness is 90% for stormwater, CSO and highway runoff samples because of the higher risk of sample failure. If completeness is not achieved, the project team will evaluate if the DQOs can still be met or if additional samples may be needed.

2.4 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through use of standard techniques to collect and analyze representative samples, along with standardized data validation and reporting procedures. By following the guidance of this QAPP, the goal of comparability between this and future sampling events will be achieved.

2.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the study goal. The concentrations of PCBs and PBDEs in whole water are anticipated to be in the pg/L to ng/L range. The analytical method detection limits presented below (Table 9) are adequately sensitive to detect PCB and PBDE congeners and other analytes at concentrations of interest to understand contaminant loadings. Based on historical data, PCB pathway averages are expected to exceed the lower calibration limits shown below in section 5 and not be subject to extensive data qualification or analytical uncertainty. PBDEs have not been previously measured in Lake Washington watershed media however the most sensitive PBDE method available has been chosen for this study.

3.0. SAMPLING DESIGN

This study is designed to collect PCB and PBDE concentration data which will be used to estimate average annual loadings. Because the study is measuring concentrations from various types of import pathways and the cost of sample analysis is high, a balance was sought between selecting sampling locations to represent spatial variability, selecting a minimum sample frequency to represent time variability in one year, and the budget limits of the grant. The design is not intended to identify sources or calculate precise loadings for any particular import pathway station (e.g., a specific CSO).

Loadings will be calculated for pathways by pooling concentration data for each pathway type and determining the average or median concentration over the sampling period (i.e. one year). Flow volume data will come from measured or modeled annual flow. The details of loadings calculations will be presented in a separate report.

All samples will be collected by KCEL staff over a one year sampling period for this study. These samples are collectively intended to represent average concentrations from six types of import pathways:

1. Major riverine inputs from the Cedar and Sammamish Rivers,
2. Major tributary streams,
3. Stormwater from municipal drainage systems,
4. Combined sewer overflows,
5. Stormwater runoff from high traffic volume roadways, and
6. Wet and dry atmospheric deposition.

In addition, ambient water samples will be collected from Lake Washington, its outflow to the Ship Canal at the Montlake Cut, and the outlet of the Lake Washington watershed to Puget Sound at the Hiram Chittenden Locks. Three samples from Lake Washington will be filtered at AXYS Analytical Services and analyzed as particulates and filtrate to provide partitioning data. One of these samples will be from the well-mixed lake stage and two from the stratified lake stage: one from the epilimnion and one from the hypolimnion.

Ambient lake, lake inlets, and outlets to be sampled bimonthly regardless of flow conditions:

1. Lake Washington
2. Montlake Cut
3. Hiram Chittenden (Ballard) Locks
4. Cedar River at USGS gauge
5. Sammamish River at 96th Ave NE.

Other inputs will be sampled quarterly. The following locations and location types will be sampled once quarterly:

1. Three major tributaries

2. Cedar River mouth
3. I-90 Bridge runoff
4. Seven stormwater discharge pipes distributed around the lake near the shoreline
5. Three CSO discharge points

The following air deposition stations will be sampled twice quarterly:

1. Sand Point Way adjacent to Magnuson Park
2. Ecology Beacon Hill weather station

Figure 7 below illustrates the locations of these features in the Greater Lake Washington drainage. The site selection process and sampling methods for this study are detailed below.

Figure 7. Sampling locations.

3.1 Site Selection

Site selection criteria were established before choosing locations to ensure sites would meet the project objectives and be logistically feasible to sample. Site selection criteria are presented in Table 5. Where site selection criteria could be met, and an existing King County monitoring station was nearby, it was selected as the exact location to sample. Sampling will also be coupled with scheduled King County water sampling where possible to maximize efficiency of sampling labor and boat costs for the study.

Table 5. Site Selection Criteria

Ship Canal and Locks	Location represents water flowing toward Puget Sound Not influenced by Locks operation
Lake	Location represents Lake Washington water not directly influenced by nearshore drainage (e.g., streams, rivers, streams or pipe discharges)
Major Rivers	Flow into Lake Washington Location is just upstream of confluence of river with Lake Washington Location is minimally impacted by lake backwater
Tributaries	Drains into Lake Washington (no tributaries drain into the Ship Canal) Reasonable accessibility for sampling Increased flows during storm events Drains a relatively large watershed compared to other tributaries
Municipal Stormwater	Drains into Lake Washington or the Ship Canal Average to large drainage basin for the jurisdiction Drains land use or land use mix that is representative of the shoreline municipalities Reasonable accessibility for sampling Ability to secure field equipment on-site Minimally influenced by backwater conditions from lake or Ship Canal
CSOs	Drains into Lake Washington or the Ship Canal Average to large drainage basin for the jurisdiction Drains land use or land use mix that is representative for the jurisdiction where site is located Reasonable accessibility for sampling Ability to secure field equipment on-site Is not considered a controlled CSO (overflow frequency of once per year or less) Overflow frequency is relatively high
Road Runoff	Location can capture runoff from a major road not co-mingled with other land uses. Reasonable accessibility for sampling Ability to secure field equipment on-site Location is accessible by vehicle instead of by boat
Air Deposition	Located away from trees and substantial buildings Located to capture prevailing winds toward Lake Washington Preferable to have weather station nearby for other collocated data (precipitation, wind patterns, etc.) Accessible yet within a secure area

Details of site selection for each of these input types are discussed below.

3.1.1 Ambient Sites

For the tributary streams and river stations, the objective is to measure concentrations in the major ambient inputs to Lake Washington. The tributaries will be sampled at their mouths during storm events when substantial stormwater input is likely to increase loadings. One baseflow event will be sampled in the dry season (July-September). King County has current water monitoring stations located at the mouths of Thornton, Juanita, and May Creeks which fit the site selection criteria and will be used for this study. Preliminary estimates of relative contributions of flow for these creeks are approximately 1%, 1%, and 2%, respectively. The Cedar and Sammamish River stations were selected to be located as close to the Lake as possible without impact by lake backwater. Both of these sites are located at existing King County monitoring stations and close to existing flow gauges (Figure 8). An additional station closer to the mouth of the Cedar River will be sampled less frequently. This station is intended to measure any additional PCB loadings from other industrial properties, such as The Boeing Company and the Renton Airport, located below the main Cedar River station. While this study is not targeting sources, the backwater effect presents a conflicting variable for siting the main sampling station at the mouth. The backwater effect is not observed during high flow events due to the gradient of the Cedar River. The same cannot be said of the backwater effect in the Sammamish River. The gradient there is much lower and inhibits accurate flow monitoring at the mouth. Thus, it will be assumed for the Sammamish River, that Swamp Creek and small industries that exist below the sampling station do not contribute significant PCBs or PBDEs loadings.

Stations in the Montlake Cut and near the Hiram Chittenden Locks were sited to capture concentrations at the outputs to Lake Washington and the Ship Canal. These stations were sited according to the site selection criteria and are located at existing King County sampling stations. The three mid-lake stations were also selected according to site selection criteria and are located at existing King County monitoring stations.

Figure 8. Rain Gauges for Determination of Storm Conditions

Table 6. Tributary, Stormwater, CSO and I-90 Sampling Site Information

Jurisdiction	Basin Name	Location	Drainage Area (ac)	General Land Use	Site name	KCEL site	Easting	Northing
Seattle	Thornton Creek	Crossing at Sand Point Way	7233	commercial / urban residential	KC station 0434	0434	1285010	257324
Kirkland	Juanita Creek	Juanita Park near mouth	4160	commercial / suburban residential	KC station 0446	0446	1299808	260356
Renton	May Creek	crossing at Lake Washington Blvd N	8977	rural / suburban and rural residential	KC station 0440	0440	1302480	196322
Seattle	Basin 067	3rd Ave NW and NW 36th St	200	urban residential	Outfall 102	NA	1263929	242005
Seattle	Basin 116	Lake Washington Blvd S at Seward Park	111	urban residential	Outfall 173	NA	1289051	203240
Seattle	Basin 081	Madrona Drive and Lake Washington Blvd	115	urban residential	No outfall name	NA	1283340	226640
Kirkland	Central Way North	N of NE 85th at 8th St	216	urban residential	8517	NA	1305335	250927
Kirkland	Moss Bay	6th St. and	180	urban residential	Moss Bay	NA	1304615	248413
Renton	Lake Washington East / North Renton	Lake Washington Blvd near Gene Coulon Park	706	commercial / urban residential / freeway	1059 / D3-12	0828JC7SB	1302558	185992
Mercer Island	Mercer Island Basin 10	Creek at N. Mercer KC pump station	231	suburban residential / light commercial	Basin #10	Mercerisl10	1294374	218771
Seattle	Henderson Street CSO	S Henderson St and Seward Park Ave S	488	urban residential	CSO Outfall 47	S081086	1286829	194166
Seattle	150 CSO	Ballard south of NW Market St on 24th Ave NW street end	392	urban residential	CSO Outfall 150	NA	1257450	247279
King County	Dexter Avenue CSO	Dexter Ave and Galer St	952	urban residential / light commercial	CSO Outfall 009	S035026	1269255	234275
Washington State Department of Transportation	I-90 Bridge segment	Eastern high rise of I-90 floating bridge	0.00085	interstate freeway	No outfall name	NA	1289394	218374

NA = not available
TBD– to be determined

3.1.2 Stormwater and Highway Runoff

Seven stormwater stations were selected across multiple shoreline cities: Kirkland, Renton, Mercer Island, and Seattle (Figure 7). Utilities staff from each city assisted with identifying access points to stormwater conveyance systems that fit the site selection criteria (Table 5). Finding adequate access points is the most challenging criterion to meet in most locations. Conveyance systems across these cities vary from stormwater ditches or creeks, such as nearly all of Mercer Island, to mixtures of creeks and pipes as utilized by the other jurisdictions.

There are a number of variables that make storm sampling challenging. Equipment security and sample chain of custody is a concern at most locations. The three stormwater stations located in Seattle will be sampled by placing equipment inside manholes. Outside of Seattle, however, sampling equipment will be placed at pipe openings or near creeks making vandalism more problematic. This may lead to more sampling attempts and time required to collect a successful sample. Another set of variables also exist related to capturing a storm sample. Because stormwater discharges were unregulated by Washington State under the National Pollutant Discharge Elimination System (NPDES) program until relatively recently (2010), very little information is available about stormwater flow. Thus, how fast the water level at a station reacts to storm intensity and duration will be initially unknown. A learning curve is expected during the first quarter of sampling after which the water level setting for autosampler triggers will be more accurately judged.

An additional variable in the stormwater sampling is the presence of some baseflow at most locations. The source and character of the baseflow is unknown. Groundwater and other infiltration is assumed to dominate, although cross-connections with sewers and other sources are potentially present. During summer months (July–September) in Seattle, storm events can be infrequent and brief. Greater rainfall is needed during these months to saturate the ground and create stormwater runoff. Therefore, stormwater discharge volume is low and the odds of collecting a stormwater discharge sample decrease. To avoid high costs associated with attempting to sample low frequency dry season storm events and gather baseflow information, one of the four samples at each stormwater station will be a baseflow sample collected during the dry season. Because there is no ground surface necessary to saturate, the highway runoff station responds quickly to dry season storm events and this location will be targeted for sampling during the dry season.

The drainage area acreage, general land use, and identifying information for the selected stormwater stations can be found in Table 6.

3.1.3 CSO

Three CSO stations were selected in Seattle owned by either Seattle or King County. Seattle and King County own the only existing CSOs that discharge to Lake Washington or the Ship Canal. A map of the King County and Seattle CSOs can be found on the King County website (http://www.kingcounty.gov/environment/wastewater/CSO/map.aspx). All of the King County CSOs that discharge to Lake Washington are “controlled” under Washington Department of Ecology’s definition (WAC 173-245) of one or less allowable untreated discharge per year. Because capturing a CSO sample during a discharge event is challenging, the frequency of

discharge needs to be higher than one or less per year to ensure successful sampling. A number of Seattle CSOs that discharge to Lake Washington are unregulated. The vast majority of these are located south of the Ship Canal (King County, 2010). For this reason, one CSO sampling station was sited on the Lake Washington shoreline, in Seattle, below the Ship Canal. Outfall 047 in the Henderson basin was selected because it has a high average frequency of discharge (>5 per year), a high annual average volume discharge (12.6 MG) (SPU 2010), and access is reasonable for sampling.

One Seattle and one King County CSO that discharge to the Ship Canal were also selected for sampling. The Seattle outfall number 150 CSO and King County Dexter CSO were selected because they are uncontrolled, they have relatively high annual average frequencies of discharge and high volumes, and have reasonable access for sampling. The Seattle 150 CSO will be sampled at a manhole, below a weir, where Ship Canal standing water exists. To account for this, the autosamplers will be adjusted to trigger above this standing water which would be substantial enough to push the Ship Canal water toward the Canal. The King County Dexter CSO will be sampled from the gate room of a regulator station which is an intrinsic (i.e., explosive) environment and thus, will require a special intrinsic autosampler that cannot be remotely triggered. This is the only location where autosamplers will not be triggered by water level. Because King County has real-time flow monitoring available for the Dexter CSO, manual triggering will not significantly decrease the likelihood of capturing a sample. Events that begin during late evening and early morning hours are more likely to be missed however.

3.1.4 Atmospheric deposition

Two atmospheric deposition stations were selected: the Beacon Hill Ecology weather station and a site on Sand Point Way near Magnuson Park (Figure 7). The Beacon Hill station was selected because it has been used to represent regional atmospheric conditions and can provide collocated weather parameters such as rainfall, wind direction, and temperature, which will assist in calculating loadings more accurately. The Sand Point Way station was also selected because it will provide atmospheric data close to lake level elevation and at the shoreline. This is expected to represent the air mass that would impact direct atmospheric deposition on Lake Washington or the Ship Canal. It is located on the Lake Washington shoreline but <5 km from the Montlake Cut. A weather station is also located < 800m from this site. A comparison of data from these two sites will determine if they can be pooled together or treated separately.

3.2 Sampling Methods

3.2.1 Ambient Lake Washington and Ship Canal waters

Lake Washington water samples will be collected and composited from three separate locations; one in the north end of Lake Washington (King County station 0826), one in the central portion (King County station 0852) and one in the southern portion (King County station 0890). The in-situ YSI profiling buoy will be used to measure the depth of the hypolimnion at a central location in the lake. A hydrolab instrument will record real time water quality data at the time of sample collection to corroborate the YSI data on the depth of the thermocline in Lake Washington. Niskin bottles will be rinsed with Lake water prior to deployment. During periods of mixing and absence of clear stratification, the lake will be subsampled at 6 depths, divided approximately evenly from 2-3 m above lake bottom to 1 meter below lake surface. During periods of stratification, six depths will be sampled from 1 m above the lake bottom, middle and top of the hypolimnion and then bottom, middle and 1m below the lake surface of the epilimnion. The three grab samples from the epilimnion will be composited with the remaining two locations to create one (epilimnetic) composite sample. The three samples from the hypolimnion will be combined in an identical fashion to create one (hypolimnetic) composite sample.

The Ship Canal sampling locations (Montlake and Hiram Chittenden Locks) will be sampled with a Scott bottle. Subsamples from 1 m above the canal bottom, the middle of the water column, and 1 m below the water surface will be composited. These two locations are not composited with each other or with Lake stations because they are expected to be much more heterogeneous than the Lake and describe potential increases in ambient PCB or PBDE concentrations from the Lake to the outlet at the Hiram Chittenden Locks. There may be a salt water intrusion of Puget Sound water into the ship canal at depth via the Hiram Chittenden Locks. Therefore, if the specific conductivity rises to more than 120% of the surface conductance, the bottom subsample will be collected from 1 m above this conductance threshold.

AXYS Analytical Services will provide proofed glass jars for use in subsampling and compositing. These activities will be performed by KCEL using cleaned glass carboys. Cleaning protocols for all equipment are described below.

3.2.2 Cedar and Sammamish River Waters

The Cedar River will be sampled in two locations (see Figure 7). The Cedar River will be sampled on a regular bimonthly schedule at the USGS gauge in Renton, WA using a 1L glass sampling bottle on a 2m pole to avoid collecting water associated with the immediate bank area. At least three dips will be collected from below the surface, composited into a pre-cleaned glass carboy and split into appropriate analytical containers. This sampling site was chosen because an established USGS flow gauge is located here and it is far enough upstream to typically avoid lake backwater effects.

The Cedar River will also be sampled quarterly 1.7 km closer to the mouth. This area has the potential to contribute additional PCB and/or PBDE inputs, but due to the backwater effects from the lake, gauging flow this close to Lake Washington is problematic. This location will also be dip sampled from the bank using a 1L glass bottle on a 2 m pole. As with the upstream Cedar

River station, at least 3 dips will be collected from below the surface and will be composited into a pre-cleaned glass carboy.

The Sammamish River will be sampled using a Scott sampler lowered off the bridge crossing at NE 96th Ave NE/Bothell Way. At least 3 grabs will be collected. When the river is greater than 3 meters depth, four grabs will be stratified between the upper 3 meters and below. These Scott bottle grabs will be composited into a pre-cleaned glass carboy and split into appropriate analytical containers. Sampling will occur during regular ambient KCEL monitoring activities.

3.2.3 Tributaries

Three tributaries will be grab-sampled near their mouths into Lake Washington, including Juanita Creek in Kirkland, May Creek in Renton and Thornton Creek in Seattle. These sampling locations coincide with existing gauging locations (Figure 8). These three urban creeks traverse a wide variety of land uses typical of the Greater Lake Washington watershed and hence are intended to represent typical or average mixed land use creek discharges to Lake Washington.

All three creeks will be sampled quarterly. There are no required antecedent dry periods. There are no additional requirements on sample timing. These streams do not have real-time flow monitoring, so KCEL professional judgment will be used to define storm conditions. Increased water depths and volumes, increased turbidity compared to base flows and greater than 0.20 inches of rainfall in the previous 12 to 24 hours will be defined as storm conditions. There are no additional requirements on sample timing because these samples are not intended to represent "first flush" or other specific events. Three quarterly samples will be conducted during storm conditions as defined above. One (3rd quarter/summertime) sample will be collected during baseflow conditions. Baseflow is defined as no measurable rainfall with the previous 48 hours and no evidence of elevated runoff or storm related turbidity. These quarterly samples will be collected by hand dipping grab samples into pre-cleaned sample containers.

3.2.4 Stormwater discharge pipes

Seven stormwater pipes will be sampled. Two wet and two dry season time-weighted composite samples will be collected at each location. The first dry season (spring quarter) sample will collect baseflow where it is present. The second dry season (summer quarter) sample will collect a dry season storm event. Locations are listed in Table 7 although unanticipated conditions may require changes particularly to CSO and stormwater pipe samplers. All stormwater pipe discharges will be sampled using composite samplers with level actuators. Level actuators will be set at suitable heights in consultation with jurisdiction recommendations to trigger sampling once discharge flows clearly exceed baseflow (if any) in each selected pipe, catch basin, or other access point. After actuation the composite samplers will pump continuously for 30 minutes on, 30 minutes off until the carboy is full. Carboys will be filled over the course of at least two hours, but no more than 12 hours. Flow characteristics of selected pipes and professional judgment will be used to select pumping rates to ensure sufficient sample volumes are obtained. Stormwater pipes will not be sampled concurrently due to equipment and staff limitations, all pipes will be targeted each quarter however.

3.2.5 Combined sewer pipes

CSOs do not discharge with enough regularity or predictability to collect actual CSO overflows. Whenever possible, actual overflow water will be sampled. However when overflows are too irregular or uncertain, samples will be collected from the combined system under conditions that represent CSO conditions by sampling higher flow / partially full conditions of combined sewers. Samples will be collected at three different CSO facilities which could overflow during rain events. Autosamplers will be set up with level actuators to collect equal time/equal volume composites. Pipe levels at which overflows may occur in certain circumstances will be established in coordination with King County or Seattle wastewater engineers. For instance, some combined sewer pipes may not be at risk of overflowing unless they are 80%+ full, while others may be at risk of overflowing at 50%+ capacity, depending on downstream conditions, pump status, and other system factors. The level actuator in each sampled pipe will be set at a height such that waters which may overflow will be collected. One King County CSO and two Seattle CSOs will be sampled. Possible locations are listed in Table 7.

3.2.6 Direct Road Runoff

Two highways cross Lake Washington via floating bridges: State Route 520 and Interstate 90. State route 99 and Interstate 5 both cross the outlet of Lake Washington to the east and west of Lake Union respectively. All of these roadways are at least 4 lanes wide and collectively have many thousands of vehicle trips per day. Due to these influences and interest in stormwater not influenced by other land uses, direct road discharge will be collected and analyzed. One sampling location will be selected in coordination with Washington State Department of Transportation (WSDOT) on the I-90 Bridge. Direct bridge runoff will be collected from a ~0.8m square well underneath a ~1.75m diameter vertical bridge deck downspout. After actuation the composite samplers will pump continuously for 30 minutes on, 30 minutes off until the carboy is filled over the course of at least 1 hour, but no more than 4 hours. Flow characteristics of the selected pipe and professional judgment will be used to select pumping rates to ensure sufficient sample volumes are obtained. If sufficient volumes are not obtained due to insufficient runoff, the sampler will be reset with revised pump settings to ensure sufficient sample volume collection during frequently re-occurring storms such as 0.20 inches of rainfall in 24hrs.

3.2.7 Air Deposition

Air deposition will be sampled as bulk (wet and dry) deposition using modifications of the method used by Brandenberger et al. (2010) to collect bulk air deposition samples for their Puget Sound air deposition study. These samplers will be fabricated at KCEL. See Appendix A for the sampler specifications and diagram.

The two sites selected for sampling are the Beacon Hill weather station and an area adjacent to Magnuson Park on Sand Point Way. The Beacon Hill weather station provides a location with an extensive history of weather data and a site considered representative of regional background in the Seattle area. The area on Sand Point Way, a few hundred meters to the west of the northern portion of the lake shoreline, also provides a nearby weather station with a history of weather data, and a northerly location that most nearly captures direct deposition to the lake.

3.2.8 Sampling Station Locations and Sample Identification

All samples will be collected by KCEL and either analyzed or shipped to AXYS Analytical Services. Thus, to best ensure secure sample tracking, this study will follow standard KCEL protocol as described in this section. Samples will be identified using a location code, a unique laboratory assigned sample number and the date of collection. This study will employ the KCEL sample tracking system which has sample labeling and identification conventions. This system creates "locators" or unique codes for each sampling location (i.e. station). Some of the stations being sampled for this study have been previously sampled by KCEL. The locators that have previously been used will also be used for this study. These can be found in Table 7. Where stations have never been sampled by KCEL, a new unique locator will be created. New locators will follow the formula:

3-digit alpha code for waterbody, basin (for CSO/stormwater) or bridge "XXX"+"-" + 3 digit alpha-numeric code for outfall ID "XXX"

The KCEL sample tracking system (LIMS) is a database that automatically creates a unique sample number following the pattern LXXXXX-01, where the last two digits correspond to the number of the sample out of the total for a sampling event (e.g., LXXXXX-02, LXXXXX-03, etc.). The five digits after the "L" are sequential following from the most recently assigned sampling event in the tracking system.

3.2.9 Sample Acquisition and Analytical Parameters

All sampling will be conducted by KCEL Environmental Services Field Science Unit (FSU). Sampling techniques are discussed in Section 3.

Each sample will be analyzed for 209 PCB congeners, select PBDE congeners and the following conventional parameters; dissolved organic carbon (DOC), total organic carbon (TOC), and total suspended solids (TSS). DOC, TOC and TSS will provide corresponding carbon fraction and solids data for PCB and PBDE concentrations. PCBs and PBDEs strongly bind to organic carbon and particles. Thus, these data will allow examination of the relationship between solids/organic carbon and sample concentrations.

KCEL SOPs do not subsample TSS with a pipette and unless solids content is such that the filter would be overwhelmed, the entire sample is used. Despite these modifications, TSS is generally considered biased low compared to mass based analysis such as suspended sediment concentrations (SSC) (Gray et al, 2000 and Gries and Sloan, 2009). This study will continue to use TSS methods to measure solids because King County has a large historical dataset of TSS concentrations and many other PCB modeling efforts have used TSS as well.

PCB and PBDE congener analysis will be conducted by AXYS Analytical Services in Sidney, British Columbia. All other analyses will be conducted by the KCEL, a Washington State Department of Ecology Certified Laboratory. A summary of stations, sampling methods and frequencies, and total sample counts is shown in Table 7 below.

Table 7. Sampling Stations and Methods and Sample Count

Sample type	Station Locations	Frequency	Field Replicates	Sampler	Method	Total Samples
Ambient Waterbodies						
Upstream Input	Cedar River at USGS gage (King County station 0438)	Bimonthly	1 @ 3 events	From bank	Surface grab with extensible pole	9
	Cedar River mouth (King County station X438)	Quarter 1 & 3	None	From bank	Surface grab with extensible pole	2
	Sammamish River (King County station B472)	Bimonthly	1 @ 3 events	Scott Bottle	Depth-integrated composite: up to two depths composited if water depth >3 meters	9
Downstream Output	Montlake Cut (King County station 0540)	Bimonthly	1 @ 3 events	Scott Bottle	Depth-integrated composite: three samples through water column depth and composite	9
	H. Chittenden Locks (King County station 0580)	Bimonthly	1 @ 3 events	Scott Bottle	Depth-integrated composite: three samples through water column depth and composite	9
Lake Washington	Composite across 3 stations (King County stations 0826, 0852, 0890)	Bimonthly	1/event when mixed; 1 @ 2 events when stratified	CTD	Depth-integrated composite (epi- and hypolimnion when stratified): 2 events during mixed, 4 events during stratified.	16[1]
Tributaries	Juanita Creek mouth (King County station 0446)	Quarterly	1/event	From bank	Grab samples composited to meet 4L volume	8
	May Creek mouth (King County station 0440)	Quarterly	1/event	From bank	Grab samples composited to meet 4L volume	8
	Thornton Creek mouth (King County station 0434)	Quarterly	1/event	From bank	Grab samples composited to meet 4L volume	8
Stormwater						
Kirkland	Central Way west of I-405	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
Kirkland	Moss Bay drainage	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
Renton	North Renton drainage near Gene Coulon Park	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
Mercer Island	N. Mercer Island drainage at KC Pump Station	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
Seattle	Fremont drainage	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
Seattle	West of Seward Park drainage	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
Seattle	Madrona drainage	Quarterly	[2]	Autosampler	Level triggered autosampler composite	4-8
CSO						
Seattle	Henderson St. CSO	Quarterly	None	Autosampler	Level triggered autosampler composite	4
Seattle	150 CSO	Quarterly	None	Autosampler	Level triggered autosampler composite	4
KC	Dexter Ave CSO	Quarterly	None	Autosampler	Level triggered autosampler composite	4
Road Runoff	I-90 bridge, east high rise	Quarterly	1/quarter	Autosampler	Level triggered autosampler composite	8
Atmospheric Deposition	Sand Point Way, near Magnuson Park	2/quarter	2/quarter[3]	Passive sampler	Bulk samples; set at 2 week intervals	15
	Beacon Hill WA Department of Ecology weather station	2/quarter	2/quarter[3]	Passive sampler	Bulk samples; set at 2 week intervals	15
Total Samples						**156**

[1]Three of these mid-lake samples will be filtered and the filtrate and particulate fractions will be analyzed separately by AXYS Analytical Services.
[2]Field replicate samples will be collected at a maximum of three rotating stations per event at locations where replication is feasible.
[3]Field replicates collected during the first two sampling quarters (4) will be sent for analysis. The remaining replicates (4) will be archived as backup and analyzed only if necessary. A volatilization loss field QC sample will substitute for one replicate sample during the first quarter.
CTD – Conductivity, Temperature, and Depth instrument used for water column sampling.

4.0. SAMPLING PROCEDURES

This section describes the sampling procedures that will be followed over the course of all sampling events to meet the study DQOs: representativeness, comparability, and completeness.

4.1 Sampler Decontamination and Sample Collection

Glass or stainless steel equipment will be used for sample collection wherever possible. Carboys, funnels, and other components will be cleaned using: (1) Alconox or other suitable laboratory detergent; (2) a DI water rinse; (3) a hexane rinse; and (4) an acetone rinse. Teflon and silicon tubing will receive this same general cleaning protocol although hexane will not be used in silicon tubing. Sampling equipment will incorporate as little silicon tubing as possible to minimize loss of target compounds to adhesion.

4.1.1 Ambient Water Samples

Ambient waters will be collected by dipping, Scott bottles, or remotely triggering Niskin bottles on a Conductivity, Temperature and Depth instrument or CTD. The grab sample bottles will be provided pre-cleaned to EPA specifications by the laboratory. The Scott sampler bottle will be laboratory cleaned using Alconox detergent and rinsed with DI water. A final rinse with on-site water will be conducted prior to sample collection. The CTD is rinsed by on-site water during descent and samples are collected during ascent.

4.1.2 Autosampling Combined Sewer Pipe, Stormwater Pipe, and Bridge Runoff Samples

Equipment and sample preparation for these sample types will generally follow Leon and Lowe (2009) protocols for constant time/constant volume autosampling (see Appendix B).

Autosamplers will be fitted with pre-cleaned silicon tubing in the peristaltic pump for each sampling event. Teflon tubing and stainless steel (SS) fittings shall be used for all other tubing runs. Teflon tubing and autosampler containers shall be cleaned with: (1) Alconox or other suitable laboratory detergent; (2) a DI water rinse; (3) a hexane rinse; and (4) an acetone rinse. All SS fittings and connectors are cleaned in the same manner. Composite autosampler bottles will be certified clean and provided by AXYS analytical laboratories.

Autosamplers will be automatically triggered by water depth in each sampled pipe.

4.1.2.1 Combined Sewer Overflow Pipes

Minimum water depth to initiate sampling will be based on professional judgement and consultation with King County wastewater and Seattle Public Utilities engineers to collect waters which may under certain pipe or pump status conditions lead to overflows. Sampling will continue as long as water depths remain above the trigger level. The sample will be collected continuously over at least 2 hours but not longer than 12 hours. The 2 hour minimum time frame was selected to balance against: (1) the risk of flows changing and representing something other

than potential CSO overflow conditions (2) the degradation of analytes in stored aliquots; and (3) a suitably long time frame to generally characterize total contaminant masses. Sample collection durations will be refined as the study progresses using the associated flow data.

4.1.2.2 Stormwater and Bridge Runoff

Trigger depths for stormwater pipes and bridge runoff samples will be determined at some level above baseflow during a rainfall event. Exact trigger points will be variable depending upon the pipe access situation and exact station situation. Stilling wells may be necessary to collect runoff prior to withdrawing samples with the autosampler. Sampling will continue as long as water depths remain above the trigger level. The sample will be collected continuously over at least 2 hours but not longer than 12 hours. The 2-hour-minimum time frame was selected to balance against: (1) the risk of sample carboys overflowing; (2) collecting insufficient sample volume from a short duration storm; (3) the degradation of analytes in stored aliquots; and (4) a suitably long time frame to generally characterize total contaminant masses. Sample collection durations will be refined as the study progresses using the associated flow data.

4.1.3 Air Deposition Samples

Due to the low field extraction efficiencies measured for PBDEs during the Puget Sound air deposition study (Brandenberger, et al. 2010), the current field study modified the sampling protocol to allow for direct analysis of rainwater including particulates. Initial QC testing will confirm that the recovery using this method is an improvement compared to the extraction efficiency reported by Brandenberger, et al. (2010). Sampling systems will be constructed by KCEL staff and include a wood framed structure supporting a funnel that drains directly into a glass bottle or carboy. The framing will be constructed to hold the collection system about 6 feet off the ground. Each structure will be constructed to support two samplers at the same time. One sampling system will be constructed for each sampling site for a total of two systems.

Each passive deposition sampler consists of the following components:

- A large stainless steel collection bowl (approximately 14 to 20 inches in diameter) with Teflon tubing attached to a nipple welded to the bottom and extended into the collection vessel.
- An amber glass collection vessel, protected from light, with a minimum volume of 4L.
- A metal or Teflon-lined cap that will secure the funnel or collection bowl to the collection vessel.
- A vent tube from the cap draining downwards.

The collection bowl and attached tubing will be cleaned at KCEL prior to deployment. The 4 L amber glass proofed sample bottles will be provided by AXYS Analytical Services.

Two samples and two replicates will be collected at each station per quarter. One replicate sample will be collected per quarter per station. The replicates from the first two quarters will be analyzed and the replicates from the third and fourth quarters will be archived for backup in case problems occur during sample analysis.

Deployment intervals will be approximately two weeks. There is no minimum rainfall requirement for a successful sample in the dry season (June–September), as it may be composed of particulate alone. However, during the wet season (October–May), a sampling period will be targeted that includes at least one rain event.

The first quarter of sampling will differ from this protocol because field QC samples will be run at each station in the replicate positions, alongside a regular sample, to test for volatilization loss. The sample collected alongside the replicate will be archived until the QC sample results are available for review and comparison to the extraction efficiency data from Battelle's Puget Sound study (Brandenberger, et al. 2010). The study will proceed with this field collection method if volatilization loss is better than Battelle's field extraction efficiency rates, with PBDE congeners 153/154 being the priority congeners for comparison. If the loss rates are not superior, the current field study will adopt the method published by Battelle with the following modifications: only one SPE disc (C18) will be used instead of two and one less GFF will therefore be needed. The resulting impact on analysis will require a solid filter extraction preparation and an addendum to this QAPP will be written.

At the time of retrieval, but before the particulate is rinsed into the sample, the volume of rainfall in each collection vessel will be estimated using a comparable container marked with 50 mL graduations. After the collected rainfall amount is recorded, a 500 mL quantity of deionized water in a Teflon squirt bottle will be used to rinse dry particulates into the collection vessel. Removal of particulates will be enhanced by brushing the funnel during rinsing with a natural hair, acetone-cleaned paintbrush (0.5–0.75-inch width). Then, the funnel will be disconnected, the collection vessel capped, and stored on ice during the return to the lab.

The entire contents of each collection vessel will be analyzed as a single sample and the results will be reported as total mass of each analyte.

4.2 Sample Delivery and Storage

All samples, grab, composite and autosampler carboys, will be kept in ice-filled coolers until delivery to KCEL on the same day that they were collected. Because autosamplers will be setup to automatically initiate sampling, samples cannot be refrigerated for the several days or weeks they may be deployed waiting for a suitable water elevation to trigger sampling or during the compositing process. Additional sample preservation, if required as shown in Table 8 below, will be performed upon receipt of the samples at KCEL. Samples will be split from the glass auto-sampler container into the appropriate analytical containers and preserved according to method specifications at the laboratory.

PCB and PBDE congener samples will be shipped to AXYS Analytical Services via overnight express delivery service. Actual shipping date may vary depending on whether additional samples are expected shortly and packaging limitations. However, the holding times are more than adequate to allow shipment to be delayed due to Friday or weekend sample collections. Table 8 shows sample handling and storage requirements.

Table 8. Sample Container, Preservation, Storage, and Hold Time Requirements

Analyte	Container	Preservation	Storage	Hold Time
Dissolved Organic	125-mL wide mouth	H_3PO_4 to pH<2[1]	refrigerate at <6°C	28 days

Carbon	amber HDPE			
Total Organic Carbon	2 x 40-mL amber VOA	H_3PO_4 to pH<2	refrigerate at <6°C	28 days
Total Suspended Solids	1-L clear wide mouth HDPE	None	refrigerate at <6°C	7 days
PCB and PBDE Congeners	4-L amber glass	None	refrigerate at <6°C in the dark	1 year
Minimum sample volume =	**4,205 mL** [2]			

[1] Within 1 day of collection, samples must be filtered (0.45 µm) prior to preservation.
[2] AXYS Analytical Services requests a minimum 3 L volume for analysis including QA samples and backup.

4.3 Chain of Custody

Chain of custody (COC) will commence at the time that grab or composite samples are collected or in the case of autosamplers, when they are deployed. Autosamplers will be secured to ensure no tampering has occurred. Thus, all samples (jars or carboys) will be under direct possession and control of King County field staff. For chain of custody purposes, locked vehicles, closed/latched storm drains, and secured autosamplers will be considered "controlled areas." All sample information will be recorded on a COC form (Figure 2). This form will be completed in the field and will accompany all samples during transport and delivery to the laboratory. Upon arrival at KCEL, the TOC, DOC, and TSS samples will be split into the appropriate containers using clean Teflon tubing then relinquished to sample login staff. The date and time of sample delivery will be recorded and both parties will sign off in the appropriate sections on the COC form at this time. Once completed, original COC forms will be archived in the project file. COC documentation will consist of the Lab's standard COC form to track release and receipt of each sample from collection to arrival at the lab. An example is attached as Appendix C.

Samples delivered after regular business hours will be stored in a secure refrigerator until the next day. Samples delivered to AXYS Analytical Services will be accompanied by a properly-completed KCEL COC form and custody seals will be placed on the shipping cooler. AXYS Analytical Services will provide a copy of the completed COC form as part of their analytical data package.

4.4 Sample Documentation

Sampling information and sample metadata will be documented using the methods noted below.

- Field sheets generated by King County's Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:
    - sample ID number
    - station name
    - in-pipe station water depth at initiation and termination of auto sampling (if applicable).

  - date and time of sample collection (or start and end times of the compositing period if applicable)
  - initials of all sampling personnel

- LIMS-generated container labels will identify each container with a unique sample number, station and site names, collect date, analyses required, and preservation method.
- The field sheet will contain records of rainfall, collection times, general weather, and the names of field crew.

4.5 Acceptance of Supplies and Consumables

Both KCEL and AXYS Analytical Services track delivery of analytical and other supplies. Reagents and other consumables are checked against method requirements and laboratory SOPs prior to acceptance. Pre-cleaned glass jars and other sample containers will be provided by AXYS Analytical Services as described in EPA Methods 1614 and 1668A. All sampling containers will be inspected by the field team members prior to use. The containers will be kept closed and in their shipping boxes until used. After sampling, the containers will be labeled, placed in coolers, chilled to 4°C, secured with chain-of-custody seals, and shipped to AXYS Analytical Services.

4.6 Field Measurements

In-situ water quality data will be automatically measured and recorded during collection of Lake Washington samples by hydrolab. These additional parameters include temperature, pH, and conductivity. These ancillary parameters will also be collected from tributaries. These parameters will be collected for at least 5 minutes from tributaries while grab samples are collected. KCEL SOP 205v4 details the procedures used for deployment of Attended Hydrolab Multiprobe Operation (Appendix D).

Flow gauges already exist for all tributary locations, and the Cedar River at Renton. Inflows to Lake Washington and outflow through the Hiram Chittenden Locks have been estimated as part of the development of a water quality model of Lake Washington by the U.S. Army Corps of Engineers (Cerco et al., 2004). These flow estimates will be used in lieu of measured flow for the Hiram Chittenden Locks and Sammamish River sampling locations due to the complexity of measuring flow through the locks and the backwater effects of Lake Washington precluding measuring flow, respectively.

Flow will be measured by established or installed gauges at all sites except in the three Seattle stormwater pipes. Where flow meters are not pre-installed, flow meters will be installed and continuously measured during the period when a sample attempt is made. The volume of rainfall collected will be measured for each air deposition sample by reading volume in the calibrated sample container before rinsing particulates into the sample. In addition, electronically recorded continuous rainfall data will be available from the weather stations located at each atmospheric deposition site.

4.7 Field Instrument Testing, Inspection, Calibration and Maintenance Frequencies

Maintenance, calibration and testing of field instruments are addressed in different KCEL SOPs. SOP 205v4 addresses Attended Hydrolab Multiprobe Operations (Appendix D) while KCEL SOP 220v3 (Appendix E) addresses maintenance, calibration, routine use, sample collection, quality control, instrument programming, data upload, reporting and review of the CTD which will be used for lake profiling.

4.8 Field Replicates

The frequency of sample replication is summarized in Table 7. For locations sampled by autosampler (CSOs, stormwater conveyance, road runoff) a field replicate will be collected during a sampling event at sites where two autosamplers can be installed. Each field replicate will be collected simultaneously by a separate auto sampler. CSOs and stormwater pipe samples may not be replicated due to space limitations at access points.

Due to the high number of stormwater stations being sampled and logistical problems with fitting two autosamplers at some stormwater pipe sampling stations, there are three replicates proposed to be sampled each event. The stations with replicates will rotate between the stations which allow replication to occur. At a minimum, the North Mercer Island, Kirkland Central Way and Renton stormwater stations will be replicated on a rotational schedule list.

For bulk atmospheric deposition sampling, one replicate will be collected at each station per sampling event. For lake and ship canal surface waters, a replicate will be collected at each station every other event for a total of three per station.

4.9 Field and Equipment Blanks

Collection and analysis of equipment/field blanks will be required for each sampling event. Analysis of field blanks is used to evaluate the levels of contamination that might be associated with the collection of samples and introduce bias into the sample result. Blanks will be collected from the following equipment:

- 2 Autosamplers
- 1 Scott bottle
- 1 Niskin bottle on the lake CTD
- 1 air deposition sampler

Field blank results for all target analytes should be consistent with the following criteria

Analyte concentrations in blank samples for PCB congeners 77, 81, 114, 123, 126, and 169 must be less than 2 pg/congener/sample, and concentrations of PCB congeners 156, 157, 167, and 189 must be less than 10 pg/congener/sample. Concentrations of all other individual PCB congeners or coelutions must be less than 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be less than 300 pg/sample.

Analyte concentrations in blank samples for BDE congeners 47,and 99 must be less than 150 pg/congener/sample. BDE congener 100 must be less than 50 pg/congener/sample and BDE congeners 181, 183, 190, 197, 203, 204, and 205 must be less than 30 pg/congener/sample. BDE congeners 206, 207, and 208 must be less than 200 pg/congener/sample and BDE congener 209 must be less than 3000 pg/congener/sample. All other congeners must be 20 pg/congener/sample.

Higher levels will be accepted when sample concentrations exceed 10 times the blank levels.

The following conditions apply to collection of the equipment / field blank sample:

- For grab samples and autosamplers, the equipment blank must be collected with the same sampling and compositing apparatus to be used to collect the samples for a given event. Each blank must be collected before the sampling begins.
- For air deposition samples an aliquot of a clean reference matrix (deionized, distilled water for water samples) is processed through the sampling equipment. Analysis of field blanks is used to evaluate the levels of contamination that might be associated with the collection of samples and introduce bias into the sample result. Field blank results for all target analytes should adhere to the above blank criteria.
- Equipment/field blanks shall be preserved, stored, and analyzed in the same manner as environmental samples.

The frequency of field blank analysis will depend on the sampling technique. For grab samples and other collection systems where new, pre-cleaned equipment are used, field blanks are required only for the first sampling event. For autosamplers where tubing and collection vessels will be re-used, field blanks may be rotated so one is collected each sampling event and at least one blank must be collected from each individual system over the course of the study.

4.10 Bulk Deposition Field QC

Because standard methods for bulk deposition are not available, bulk samplers have been constructed to collect both wet and dry deposition. Additional QC samples will be collected for this matrix to evaluate their capabilities. These procedures involve wipe tests after the de-ionized water flush is conducted to evaluate the efficiency of the brushing and flushing at removing dry deposition from the funnel walls. A field spike sample will also be deployed as described below to measure potential loss of analytes from the sampler due to re-volatization.

4.10.1 Dry Deposition QC Samples

While wet deposition collection efficiency is assumed to be 100%, dry deposition collection efficiency for the bulk samplers is currently unknown. To understand the potential loss or selective sampling of dry particulates with the bulk samplers, two wipe tests of the funnel will be conducted after the dry particulates are brushed and flushed into the collection vessel. Wipe tests will occur once during the first quarter and again in the second quarter. Wipes are saturated with either hexane or isopropanol. They are proofed and supplied by AXYS Analytical Services. One half of the interior surface area of the bulk deposition funnel will be swabbed with the wipe.

The mass of PCBs and PBDEs congeners in the wipe will be reported to the solids levels shown below (Tables 9 and 10). Individual congener and sum of congener sampling loss due to inadequate flushing and/or brushing, such as adhering to the funnel and collection tubing are expected to be less than 25% of individual congeners and the sum of PCB and PBDE congeners.

Table 9. Congener Concentrations in Target Spikes for Air Deposition Re-volatilization QC Samples

Analyte	Typical Detection Limit/SDL	LMCL based on CS-1
CL1-PCB-1	1	20
CL1-PCB-2	1	20
CL1-PCB-3	1	20
CL2-PCB-4	2	20
CL2-PCB-5	2	20
CL2-PCB-6	2	20
CL2-PCB-7	2	20
CL2-PCB-8	2	20
CL2-PCB-9	2	20
CL2-PCB-10	2	20
CL2-PCB-11	2	20
CL2-PCB-12/13	2	40
CL2-PCB-14	2	20
CL2-PCB-15	2	20
CL3-PCB-16	1	20
CL3-PCB-17	1	20
CL3-PCB-19	1	20
CL3-PCB-21/33	1	40
CL3-PCB-22	1	20
CL3-PCB-23	1	20
CL3-PCB-24	1	20
CL3-PCB-25	1	20
CL3-PCB-26/29	1	40
CL3-PCB-27	1	20
CL3-PCB-28/20	1	40
CL3-PCB-30/18	1	40
CL3-PCB-31	1	20
CL3-PCB-32	1	20
CL3-PCB-34	1	20
CL3-PCB-35	1	20
CL3-PCB-36	1	20
CL3-PCB-37	1	20
CL3-PCB-38	1	20
CL3-PCB-39	1	20
CL4-PCB-41/40/71	1	60
CL4-PCB-42	1	20
CL4-PCB-43	1	20
CL4-PCB-44/47/65	1	60
CL4-PCB-45/51	1	40
CL4-PCB-46	1	20
CL4-PCB-48	1	20

Analyte	Typical Detection Limit/SDL	LMCL based on CS-1
CL4-PCB-50/53	1	40
CL4-PCB-52	1	20
CL4-PCB-54	1	20
CL4-PCB-55	1	20
CL4-PCB-56	1	20
CL4-PCB-57	1	20
CL4-PCB-58	1	20
CL4-PCB-59/62/75	1	60
CL4-PCB-60	1	20
CL4-PCB-61/70/74/76	1	80
CL4-PCB-63	1	20
CL4-PCB-64	1	20
CL4-PCB-66	1	20
CL4-PCB-67	1	20
CL4-PCB-68	1	20
CL4-PCB-69/49	1	40
CL4-PCB-72	1	20
CL4-PCB-73	1	20
CL4-PCB-77	1	20
CL4-PCB-78	1	20
CL4-PCB-79	1	20
CL4-PCB-80	1	20
CL4-PCB-81	1	20
CL5-PCB-82	1	20
CL5-PCB-83/99	1	40
CL5-PCB-84	1	20
CL5-PCB-88/91	1	40
CL5-PCB-89	1	20
CL5-PCB-92	1	20
CL5-PCB-94	1	20
CL5-PCB-95/100/93/102/98	1	100
CL5-PCB-96	1	20
CL5-PCB-103	1	20
CL5-PCB-104	1	20
CL5-PCB-105	1	20
CL5-PCB-106	1	20
CL5-PCB-107/124	1	40
CL5-PCB-108/119/86/97/125/87	1	120
CL5-PCB-109	1	20
CL5-PCB-110/115	1	40
CL5-PCB-111	1	20
CL5-PCB-112	1	20
CL5-PCB-113/90/101	1	60
CL5-PCB-114	1	20
CL5-PCB-117/116/85	1	60
CL5-PCB-118	1	20
CL5-PCB-120	1	20

Analyte	Typical Detection Limit/SDL	LMCL based on CS-1
CL5-PCB-121	1	20
CL5-PCB-122	1	20
CL5-PCB-123	1	20
CL5-PCB-126	1	20
CL5-PCB-127	1	20
CL6-PCB-128/166	1	40
CL6-PCB-130	1	20
CL6-PCB-131	1	20
CL6-PCB-132	1	20
CL6-PCB-133	1	20
CL6-PCB-134/143	1	40
CL6-PCB-136	1	20
CL6-PCB-137	1	20
CL6-PCB-138/163/129/160	1	80
CL6-PCB-139/140	1	40
CL6-PCB-141	1	20
CL6-PCB-142	1	20
CL6-PCB-144	1	20
CL6-PCB-145	1	20
CL6-PCB-146	1	20
CL6-PCB-147/149	1	40
CL6-PCB-148	1	20
CL6-PCB-150	1	20
CL6-PCB-151/135/154	1	60
CL6-PCB-152	1	20
CL6-PCB-153/168	1	40
CL6-PCB-155	1	20
CL6-PCB-156/157	1	40
CL6-PCB-158	1	20
CL6-PCB-159	1	20
CL6-PCB-161	1	20
CL6-PCB-162	1	20
CL6-PCB-164	1	20
CL6-PCB-165	1	20
CL6-PCB-167	1	20
CL6-PCB-169	1	20
CL7-PCB-170	1	20
CL7-PCB-171/173	1	40
CL7-PCB-172	1	20
CL7-PCB-174	1	20
CL7-PCB-175	1	20
CL7-PCB-176	1	20
CL7-PCB-177	1	20
CL7-PCB-178	1	20
CL7-PCB-179	1	20
CL7-PCB-180/193	1	40
CL7-PCB-181	1	20

Analyte	Typical Detection Limit/SDL	LMCL based on CS-1
CL7-PCB-182	1	20
CL7-PCB-183/185	1	40
CL7-PCB-184	1	20
CL7-PCB-186	1	20
CL7-PCB-187	1	20
CL7-PCB-188	1	20
CL7-PCB-189	1	20
CL7-PCB-190	1	20
CL7-PCB-191	1	20
CL7-PCB-192	1	20
CL8-PCB-194	1	20
CL8-PCB-195	1	20
CL8-PCB-196	1	20
CL8-PCB-197/200	1	40
CL8-PCB-198/199	1	40
CL8-PCB-201	1	20
CL8-PCB-202	1	20
CL8-PCB-203	1	20
CL8-PCB-204	1	20
CL8-PCB-205	1	20
CL9-PCB-206	1	20
CL9-PCB-207	1	20
CL9-PCB-208	1	20
CL10-PCB-209	1	20

Table 10. Congener Concentrations in Target Spikes for Air Deposition Re-volatilization QC Samples

PCB Congeners	Congener No.	Concentration of Standard Solution (ng/mL)
2-MoCB	1	1
4-MoCB	3	1
2,2'-DiCB	4	1
4,4'-DiCB	15	1
2,2',6-TriCB	19	1
2,3,5-TriCB	23	1
2',3,5-TriCB	34	1
3,4,4'-TriCB	37	1
2,2',6,6'-TeCB	54	1
3,3',4,4'-TeCB	77	1
3,4,4',5-TeCB	81	1
2,2',4,6,6'-PeCB	104	1
2,3,3',4,4'-PeCB	105	1
2,3,4,4',5-PeCB	114	1
2,3',4,4',5-PeCB	118	1
2',3,4,4',5-PeCB	123	1

PCB Congeners	Congener No.	Concentration of Standard Solution (ng/mL)
3,3',4,4',5-PeCB	126	1
2,2',4,4',6,6'-HxCB	155	1
2,3,3',4,4',5-HxCB	156	1
2,3,3',4,4',5'-HxCB	157	1
2,3',4,4',5,5'-HxCB	167	1
2-3,3',4,4',5,5'-HxCB	169	1
2,2',3,3',4,4',5-HpCB	170	1
2,2',3,4,4',5,5'-HpCB	180	1
2,2',3,4,4',5,6'-HpCB	182	1
2,2',3,4',5,5',6-HpCB	187	1
2,2',3,4',5,6,6'-HpCB	188	1
2,3,3',4,4',5,5'-HpCB	189	1
2,2',3,3',5,5',6,6'-OcCB	202	1
2,3,3',4,4',5,5',6-OcCB	205	1
2,2',3,3',4,4',5,5',6-NoCB	206	1
2,2',3,3',4,5,5',6,6'-NoCB	208	1
2,2',3,3',4,4',5,5',6,6'-DeCB	209	1
PBDE Congeners		
2,4-DiBDE	7	5
2,4'-DiBDE	8	5
2,6-DiBDE	10	5
3,3'-DiBDE	11	5
3,4-DiBDE	12	5
3,4'-DiBDE	13	5
4,4'-DiBDE	15	5
2,2',4-TrBDE	17	5
2,3',4-TrBDE	25	5
2,4,4'-TrBDE*	28	5
2,4,6-TrBDE	30	5
2,4',6-TrBDE	32	5
2',3,4-TrBDE	33	5
3,3',4-TrBDE	35	5
3,4,4'-TrBDE	37	5
2,2',4,4'-TeBDE*	47	5
2,2',4,5'-TeBDE	49	5
2,2',4,6'-TeBDE	51	5
2,3',4,4'-TeBDE	66	5
2,3',4',6-TeBDE	71	5
2,4,4',6-TeBDE	75	5
3,3',4,4'-TeBDE	77	5
3,3',4,5'-TeBDE	79	5
2,2',3,4,4'-PeBDE	85	5
2,2',4,4',5-PeBDE*	99	5
2,2',4,4',6-PeBDE*	100	5
2,3,3',4,4'-PeBDE	105	5
2,3,4,5,6-PeBDE	116	5

PCB Congeners	Congener No.	Concentration of Standard Solution (ng/mL)
2,3',4,4',6-PeBDE	119	5
2,3',4,5,5'-PeBDE	120	5
3,3',4,4',5-PeBDE	126	5
3,3',4,4',5-PeBDE	128	5
2,2',3,4,4',5'-HxBDE	138	5
2,2',3,4,4',6'-HxBDE	140	5
2,2',4,4',5,5'-HxBDE*	153	5
2,2',4,4',5',6-HxBDE*	154	5
2,2',4,4',6,6'-HxBDE	155	5
2,3,4,4',5,6-HxBDE	166	5
2,2',3,4,4',5,6-HpBDE	181	5
2,2',3,4,4',5',6-HpBDE*	183	5
2,3,3',4,4',5,6-HpBDE	190	5
2,2',3,3',4,4',6,6'-OcBDE	197	5
2,2',3,4,4',5,5',6-OcBDE	203	5
2,2',3,4,4',5,6,6'-OcBDE	204	5
2,3,3',4,4',5,5',6-OcBDE	205	5
2,2',3,3',4,4',5,5',6-NoBDE	206	5
2,2',3,3',4,4',5,6,6'-NoBDE	207	5
2,2',3,3',4,5,5',6,6'-NoBDE	208	5
2,2',3,3',4,4',5,5',6,6'-DeBDE*	209	50

4.10.2 Wet Deposition QC Samples

Because bulk samplers will be field deployed for approximately two weeks and analytes of interest may be lost during deployment, field loss QC samples will be collected. A 1L aliquot of de-ionized water will be spiked with 1mL of PCB standard solution and 0.2mL of PBDE standard solution. This field spike will be deployed in the first quarter with the collection vessel wrapped in aluminum foil just as bulk deposition samplers, but with both the inlet tubing clamped closed. Vent tubing will remain open. The spike will remain exposed in the field for two weeks to equilibrate. At the conclusion of the two-week field period, the inlet tubing clamp will be removed and one headspace volume of air will be vacuumed from the collection vessel with a peristaltic pump. The headspace air will be discarded and the collection vessel will be returned to the lab and decanted into sampling containers just as environmental samples are treated. Volatilization loss rates from the collection vessel should be less than 20% of the spiked mass.

A second sampler recovery sample will be conducted using the same procedures and spike concentrations as above. This spiked water sample will be poured through the bulk deposition sample apparatus and then immediately split into appropriate analytical containers. This QC sample will be used to evaluate the loss of analytes of interest from evaporation from or adhesion to the stainless steel funnel and/or tubing of the bulk deposition sampler.

5.0. ANALYTICAL METHODS AND DETECTION LIMITS

Analytical methods for PCB and PBDE congeners and conventional analyses are presented in this section, along with analyte-specific detection limits. For the PCB and PBDE congeners, and selected conventional analytes, the terms MRL and PQL, used in the following subsections, refer to method reporting limit and practical quantitation limit, respectively. The MRL is defined as the *minimum concentration of a chemical constituent that can be reliably determined with 99% confidence to be greater than zero based on analysis of a minimum of 7 replicate matrix spikes at 1-5 times the estimated detection limits* (40 CFR Part 136.2), while the PQL is defined as *the minimum concentration of a chemical constituent that can be reliably quantified within specified limits of precision and accuracy during routine laboratory operating conditions* (50 FR 46906, November 13, 1985). For high resolution isotopic dilution based methods, these terms are less applicable because limits of quantitation are derived from calibration capabilities and inevitable but typically low level equipment and laboratory blank contamination.

Additional reporting limit terms used particularly for PCB and PBDE congener analyses are sample specific detection limits and lowest method calibration limits. Sample specific detection limit (SDL) is determined by converting the area equivalent to 2.5 times the estimated chromatographic noise height to a concentration. SDLs are determined individually for every congener, of each sample analysis run and accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Lowest method calibration limits (LMCL) are based on calibration points from standard solutions. They are prorated by sample size and are supported by statistically-derived MRL values.

The PCB and PBDE congener data will be reported to LMCLs and flagged down to the SDL value. In many cases the SDL may be below the LMDL. Method 1668A defines a Minimum Level (ML) value for each congener. The ML value is used to evaluate levels in the method blank. The ML is based on the lowest method calibration limit (LMCL) and any laboratory performing the method should be able to achieve at least that level. AXYS Analytical Services uses an additional lower calibration point lower than the calibration points specified in the method so is able to quantify congeners below the ML specified in the method. See Table 12 and Table 14 for congener-specific LMCLs for PCB and PBDE congeners.

Samples will be analyzed as whole water without filtration except for three samples from mid-Lake Washington which will be filtered prior to analysis. Both the solids and the filtrate will be analyzed for PCBs and PBDEs using the same methods described below for water samples. These data will be used to determine a partitioning coefficient for the fate and transport model that will be applied to PCBs entering Lake Washington. The fate and transport model will apply a partitioning coefficient to PCBs entering the lake, regardless of pathway, to determine what proportion settles as sediment on the bottom of the lake or resides in the dissolved state. Thus, only samples from the mid-lake composites will be analyzed for particulates.

5.1 PCB Congeners in Waters and QC Wipe Samples (i.e. Solids)

PCB congener analysis will follow EPA Method 1668A Revision A (EPA 2003), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. AXYS Analytical Services will be switching to Revision C of Method 1668 during this project. This method provides reliable analyte identification and very low detection limits. An extensive suite of labeled surrogate standards (Table 11) is added before samples are extracted. Data are "recovery-corrected" for losses in extraction and clean-up, and analytes are quantified against their labeled analogues. The principle differences between Method 1668a and 1668c are the replacement of individual laboratory acceptable criteria with interlaboratory developed acceptance criteria. This change is not anticipated to modify result values although there may be minor differences in data qualifiers not affecting usability.

AXYS Analytical Services will perform this analysis according to their Standard Operating Procedure MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668 (Appendix F). A one-liter sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil, and Alumina. Analysis is performed with an SPB Octyl column and a secondary DB1 column is used to resolve the co-eluting congeners PCB156 and PCB157. Method 1668A requires that if a sample contains more than 1% total solids (measured by mass at AXYS Analytical Services), the solids and liquid will be extracted separately and extracts combined for analysis.

Table 11. Labeled Surrogates and Recovery Standards Used for EPA Method 1668A PCB Congener Analysis by IUPAC[1] congener number

C_{13}-labeled PCB Surrogate Standards				
1	37	123	155	202
3	54	118	167	205
4	81	114	156/157	208
15	77	105	169	206
19	104	126	188	209
C_{13}-labeled Cleanup Standards				
28	111	178		
C_{13}-labeled Internal (Recovery) Standards				
9	52	101	138	194

[1]International Union of Pure and Applied Chemistry

In addition to the surrogate, cleanup, and internal standards, which assess sample accuracy and bias, a method blank, and an ongoing precision and recovery sample will be analyzed with each set of samples. Note that a matrix spike and matrix spike duplicate are not required, nor meaningful under Method 1668A.

- A method blank is an aliquot of a clean reference matrix (lab reagent water for water samples) that is processed through the entire analytical procedure. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results for all target analytes should meet the criteria specified in section 3.7 for blank levels. Method 1668A has specific requirements for method blanks that must be met before sample data can be reported (see section 9.5.2 of Method 1668A).
- An ongoing precision and recovery (OPR) sample is to be analyzed with each QC sample batch. The OPR samples must show acceptable recoveries, according to Method 1668A, in order for sample data to be reported without flags.

Table 12 lists the 209 PCB congeners and their respective target SDL and LMCL values. The reporting limits for individual samples may differ from those in Table 12 since they are determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown. Note that several of the congeners co-elute and a single SDL or LMCL value is provided for the congeners in aggregate.

Table 12. PCB Congener water detection limits and lower calibration limits by EPA method 1668A, AXYS Analytical Services method MLA 010. Values in pg/L (or pg/sample for air deposition) based on 1 L sample but will be prorated for actual sample size.

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
CL1-PCB-1	1.0	4.0
CL1-PCB-2	1.0	4.0
CL1-PCB-3	1.0	4.0
CL2-PCB-4	2.0	4.0
CL2-PCB-5	2.0	4.0
CL2-PCB-6	2.0	4.0
CL2-PCB-7	2.0	4.0
CL2-PCB-8	2.0	4.0
CL2-PCB-9	2.0	4.0
CL2-PCB-10	2.0	4.0
CL2-PCB-11	2.0	4.0
CL2-PCB-12/13	2.0	8.0
CL2-PCB-14	2.0	4.0
CL2-PCB-15	2.0	4.0
CL3-PCB-16	1.0	4.0
CL3-PCB-17	1.0	4.0
CL3-PCB-19	1.0	4.0
CL3-PCB-21/33	1.0	8.0
CL3-PCB-22	1.0	4.0
CL3-PCB-23	1.0	4.0
CL3-PCB-24	1.0	4.0
CL3-PCB-25	1.0	4.0
CL3-PCB-26/29	1.0	8.0
CL3-PCB-27	1.0	4.0
CL3-PCB-28/20	1.0	8.0
CL3-PCB-30/18	1.0	8.0
CL3-PCB-31	1.0	4.0
CL3-PCB-32	1.0	4.0
CL3-PCB-34	1.0	4.0
CL3-PCB-35	1.0	4.0
CL3-PCB-36	1.0	4.0
CL3-PCB-37	1.0	4.0
CL3-PCB-38	1.0	4.0
CL3-PCB-39	1.0	4.0
CL4-PCB-41/40/71	1.0	12.0

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
CL4-PCB-42	1.0	4.0
CL4-PCB-43	1.0	4.0
CL4-PCB-44/47/65	1.0	12.0
CL4-PCB-45/51	1.0	8.0
CL4-PCB-46	1.0	4.0
CL4-PCB-48	1.0	4.0
CL4-PCB-50/53	1.0	8.0
CL4-PCB-52	1.0	4.0
CL4-PCB-54	1.0	4.0
CL4-PCB-55	1.0	4.0
CL4-PCB-56	1.0	4.0
CL4-PCB-57	1.0	4.0
CL4-PCB-58	1.0	4.0
CL4-PCB-59/62/75	1.0	12.0
CL4-PCB-60	1.0	4.0
CL4-PCB-61/70/74/76	1.0	16.0
CL4-PCB-63	1.0	4.0
CL4-PCB-64	1.0	4.0
CL4-PCB-66	1.0	4.0
CL4-PCB-67	1.0	4.0
CL4-PCB-68	1.0	4.0
CL4-PCB-69/49	1.0	8.0
CL4-PCB-72	1.0	4.0
CL4-PCB-73	1.0	4.0
CL4-PCB-77	1.0	4.0
CL4-PCB-78	1.0	4.0
CL4-PCB-79	1.0	4.0
CL4-PCB-80	1.0	4.0
CL4-PCB-81	1.0	4.0
CL5-PCB-82	1.0	4.0
CL5-PCB-83/99	1.0	8.0
CL5-PCB-84	1.0	4.0
CL5-PCB-88/91	1.0	8.0
CL5-PCB-89	1.0	4.0
CL5-PCB-92	1.0	4.0
CL5-PCB-94	1.0	4.0
CL5-PCB-95/100/93/102/98	1.0	20.0
CL5-PCB-96	1.0	4.0
CL5-PCB-103	1.0	4.0

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
CL5-PCB-104	1.0	4.0
CL5-PCB-105	1.0	4.0
CL5-PCB-106	1.0	4.0
CL5-PCB-107/124	1.0	8.0
CL5-PCB-108/119/86/97/125/87	1.0	24.0
CL5-PCB-109	1.0	4.0
CL5-PCB-110/115	1.0	8.0
CL5-PCB-111	1.0	4.0
CL5-PCB-112	1.0	4.0
CL5-PCB-113/90/101	1.0	12.0
CL5-PCB-114	1.0	4.0
CL5-PCB-117/116/85	1.0	12.0
CL5-PCB-118	1.0	4.0
CL5-PCB-120	1.0	4.0
CL5-PCB-121	1.0	4.0
CL5-PCB-122	1.0	4.0
CL5-PCB-123	1.0	4.0
CL5-PCB-126	1.0	4.0
CL5-PCB-127	1.0	4.0
CL6-PCB-128/166	1.0	8.0
CL6-PCB-130	1.0	4.0
CL6-PCB-131	1.0	4.0
CL6-PCB-132	1.0	4.0
CL6-PCB-133	1.0	4.0
CL6-PCB-134/143	1.0	8.0
CL6-PCB-136	1.0	4.0
CL6-PCB-137	1.0	4.0
CL6-PCB-138/163/129/160	1.0	16.0
CL6-PCB-139/140	1.0	8.0
CL6-PCB-141	1.0	4.0
CL6-PCB-142	1.0	4.0
CL6-PCB-144	1.0	4.0
CL6-PCB-145	1.0	4.0
CL6-PCB-146	1.0	4.0
CL6-PCB-147/149	1.0	8.0
CL6-PCB-148	1.0	4.0
CL6-PCB-150	1.0	4.0
CL6-PCB-151/135/154	1.0	12.0
CL6-PCB-152	1.0	4.0

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
CL6-PCB-153/168	1.0	8.0
CL6-PCB-155	1.0	4.0
CL6-PCB-156/157	1.0	8.0
CL6-PCB-158	1.0	4.0
CL6-PCB-159	1.0	4.0
CL6-PCB-161	1.0	4.0
CL6-PCB-162	1.0	4.0
CL6-PCB-164	1.0	4.0
CL6-PCB-165	1.0	4.0
CL6-PCB-167	1.0	4.0
CL6-PCB-169	1.0	4.0
CL7-PCB-170	1.0	4.0
CL7-PCB-171/173	1.0	8.0
CL7-PCB-172	1.0	4.0
CL7-PCB-174	1.0	4.0
CL7-PCB-175	1.0	4.0
CL7-PCB-176	1.0	4.0
CL7-PCB-177	1.0	4.0
CL7-PCB-178	1.0	4.0
CL7-PCB-179	1.0	4.0
CL7-PCB-180/193	1.0	8.0
CL7-PCB-181	1.0	4.0
CL7-PCB-182	1.0	4.0
CL7-PCB-183/185	1.0	8.0
CL7-PCB-184	1.0	4.0
CL7-PCB-186	1.0	4.0
CL7-PCB-187	1.0	4.0
CL7-PCB-188	1.0	4.0
CL7-PCB-189	1.0	4.0
CL7-PCB-190	1.0	4.0
CL7-PCB-191	1.0	4.0
CL7-PCB-192	1.0	4.0
CL8-PCB-194	1.0	4.0
CL8-PCB-195	1.0	4.0
CL8-PCB-196	1.0	4.0
CL8-PCB-197/200	1.0	8.0
CL8-PCB-198/199	1.0	8.0
CL8-PCB-201	1.0	4.0
CL8-PCB-202	1.0	4.0

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
CL8-PCB-203	1.0	4.0
CL8-PCB-204	1.0	4.0
CL8-PCB-205	1.0	4.0
CL9-PCB-206	1.0	4.0
CL9-PCB-207	1.0	4.0
CL9-PCB-208	1.0	4.0
CL10-PCB-209	1.0	4.0

SDL = sample detection limit
LMCL = lower method calibration limit
pg/L = picograms per liter

5.2 PBDE Congeners in Waters and QC Wipe Samples (i.e. Solids)

PBDE congener analysis will be determined by EPA Method 1614 (EPA 2003), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification similar to Method 1668A for PCBs. This method provides reliable analyte identification and very low detection limits. An extensive suite of labeled surrogate standards (Table 13) is added before samples are extracted. Data are "recovery-corrected" for losses in extraction and cleanup, and analytes are quantified against their labeled analogues or a related labeled compound.

AXYS Analytical Services will perform this analysis according to their Standard Operating Procedure MLA-033 Analytical Method for the Determination of 46 PBDE Congeners by EPA Method 1614 (Appendix G). A one-liter sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil, and Alumina. Method 1614 requires that if a sample contains more than 1% total solids, the solids and liquid will be extracted separately and the extracts combined for analyses.

Table 13. Labeled Surrogates and Recovery Standards Used for EPA Method 1614 PBDE Congener Analysis

C_{13}-labeled PBDE Congener Surrogate Standards	
28	153
47	154
99	183
100	209
C_{13}-labeled Cleanup Standards	
139	
C_{13}-labeled Internal (Recovery) Standards	
52	138

In addition to the surrogate, cleanup, and internal standards, which control sample accuracy and bias, a method blank, and an ongoing precision and recovery sample will be analyzed with each set samples. Note that a matrix spike and matrix spike duplicate are not required, nor meaningful under Method 1614.

- A **method blank** is an aliquot of a clean reference matrix (deionized, distilled water for water samples) that is processed through the entire analytical procedure. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results for all target analytes should be "less than the ML." Method 1614 has specific requirements for method blanks that must be met before sample data can be reported (see section 9.5.2 of Method 1614).
- An **ongoing precision and recovery** (OPR) sample is to be analyzed with each QC sample batch. The OPR samples must show acceptable recoveries, according to Method 1614, in order for sample data to be reported without flags.

Table 14 lists the 40 PBDE congeners and their respective target MRL values. The reported SDLs for individual samples may differ from those in Table 14 since they are determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown. Note that several of the congeners co-elute and a single result or MRL value is provided for the congeners in aggregate.

Table 14. PBDE Congener water sample detection limits and lower calibration limits by EPA method 1614A, AXYS Analytical Services method MLA 033. Values in pg/L (or pg/sample for air deposition).

PBDE Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
BR3-DPE-28/33	10.0	50.0
BR4-DPE-47	10.0	50.0
BR5-DPE-99	10.0	50.0
BR5-DPE-100	10.0	50.0
BR6-DPE-153	10.0	50.0
BR6-DPE-154	10.0	50.0
BR7-DPE-183	20.0	50.0
BR10-DPE-209	200	500.0

SDL = sample detection limit
LMCL = lower method calibration limit
pg/L = picograms per liter

5.3 Conventionals

All conventional analyses will follow Standard Methods (SM) protocols (American Public Health Association [APHA] 1998). Table 15 presents the analytical methods, detection limits and units for conventional analyses.

Table 15. Conventionals Analytical Methods and Detection Limits in mg/L

Analyte	Method	MRL	PQL
Dissolved Organic Carbon	SM5310-B	0.5	1.0
Total Organic Carbon	SM5310-B	0.5	1.0
Total Suspended Solids	SM2540-D	0.5	1.0

Dissolved and total organic carbon will be analyzed according to SM5310-B, which is high-temperature combustion with infrared spectroscopy. Total suspended solids analyses will be performed according to SM2540-D, which is a gravimetric determination. Table 16 describes the minimum QC required for the conventionals analyses.

Table 16. Conventionals QA/QC Frequency and Acceptance Criteria for Water Samples

Frequency	Method Blank 1 per batch*	Lab Duplicate (RPD) 1 per batch*	Spike Blank (% Recovery) 1 per batch*	Matrix Spike (% Recovery) 1 per batch*	LCS (% Recovery) 1 per batch*	Check Standard (% Recovery) per batch*
Total Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%	N/A
Dissolved Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%	N/A
Total Suspended Solids	<MDL	25%	N/A	N/A	80-120%	N/A

* batch = 20 samples or less prepared as a set
< MDL = less than the Method Detection Limit.
RPD = Relative Percent Difference
LCS = Lab Control Sample
N/A = Not Applicable

Quality control samples analyzed in association with conventional analyses will include method blanks, laboratory duplicates, matrix spikes, spike blanks, and laboratory control samples, as shown above in Table 16. Conventional QC samples will be analyzed at the frequency of one per QC batch, which is up to 20 samples prepared and analyzed together as a set.

- A **method blank** is an aliquot of a clean reference matrix (deionized, distilled water for water samples) that is processed through the entire analytical procedure. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory. Method blank results for all target analytes should be “less than the MRL” for conventional analyses.

- A **laboratory duplicate** is a second aliquot of sample matrix that is processed through the entire analytical procedure along with the original sample in the same quality control batch. For conventional analyses, the laboratory duplicate aliquots are all analyzed on matrix taken from a single sample container, with the exception of TOC. Laboratory duplicate results are used to assess the precision of the analytical method and the relative percent difference of the results should be within method-specified or performance-based quality control limits.
- A **matrix spike** is a known concentration of one or more target analytes, which is introduced into a second aliquot of one analytical sample. The spiked sample is processed through the entire analytical procedure. Analysis of the matrix spike is used as an indicator of sample matrix effect on the recovery of target analytes and, thus, potential bias introduced into the sample results. Quality control limits are based on the percent recovery of the spiked compounds and are either method-specific or performance-based.

Table 16, above, details the frequencies of QC samples required for conventional analyses. In general, for all methods except the PCB congener analysis, this frequency is 1 in 20 samples or 1 per batch, whichever is more frequent.

5.4 Laboratory Instrument Testing, Inspection, Calibration and Maintenance Frequency

For PCB and PBDE analysis, instrument calibration and testing is integral with their respective methods (EPA 2003 and EPA, 2007b). For TOC and DOC, calibration standards and other required and as-needed maintenance frequencies are addressed in KCEL SOP 336v4 for these methods (Appendix H). These issues are addressed for TSS in KCEL SOP 309v3 (Appendix I).

6.0. SPECIAL TRAINING AND CERTIFICATION

This project requires some special training for field sampling staff and certification by the laboratories conducting sample analyses. Confined space entry will be necessary for some of the stormwater and CSO sampling in this project. KCEL staff, and only staff with appropriate training, will perform all confined space entry sampling.

KCEL is a Washington State Department of Ecology accredited laboratory and will conduct all the sampling as well as conventional parameter analyses. AXYS Analytical Services in British Columbia, Canada is accredited with Canadian Association for Laboratory Accreditation Inc. and multiple United States accreditation programs including the Washington Department of Ecology. AXYS quality policies meet or exceed the ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories." AXYS Analytical Laboratories will be subcontracted for the PCB and PBDE congener sample analyses because they are capable of meeting the data quality objectives for this project.

7.0. DATA VALIDATION, REPORTING AND RECORD KEEPING

Due to the specialized, contracted, methods employed for the PCB and PBDE analysis, King County will conduct additional data validation on the PCB and PBDE congener data. The other data will receive standard KCEL validation but full documentation will be maintained in the file should more detailed, external review be necessary.

7.1 Data Validation

Data validation is critical for evaluating how well analytical data meet project DQOs. Data validation is performed during several steps in the process of sample analysis. Data validation will be performed by the King County Field Study Technical Lead (Richard Jack) by reviewing complete data packages supplied both by AXYS Analytical Services and KCEL. PCB and PBDE congeners will be validated according to EPA protocols (EPA 2001 and 2005), modified appropriately for their respective methods. EPA data validation guidelines are not available for conventional water quality data. Conventional data will be verified and validated against reference method requirements and the QC requirements provided in this SAP. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records. PCB and PBDE congener data will be flagged as appropriate according to EPA method specific guidance. In particular, method and equipment blank contamination will be used together to understand the sources of contamination, their relative contributions to environmental samples, and environmental heterogeneity.

In addition, the project manager will assess data quality by reviewing all QA anomalies reported by the KCEL QA Officer and judging use of flagged data for project specific purposes. This data quality assessment and reconciliation with project requirements will include data collected under this QAPP along with all historic sediment and fish tissue used in the project.

7.2 Reporting

Per contract requirements, semi-annual status reports will be given to EPA by the Project Manager. PCB/PBDE congener samples will be shipped to AXYS Analytical Services at KCEL's discretion, based on weather patterns and packaging. The expected turn-around time for congener analysis is 60 to 90 days from receipt. The turn-around time for all other analytical data is approximately six to eight weeks from the date of sample collection. It is anticipated that data from all sampling events will be validated, reviewed, and ready for release by summer 2012. A data report will be submitted to EPA in July 2012.

7.3 Record Keeping and Data Management

All hard-copy field sampling records, custody documents, raw lab data, and laboratory summaries and narratives will be archived according to KCEL policy for a minimum of 10 years from the date samples were collected. These records will include both hard copy and electronic data received from AXYS Analytical Services. Conventional, analytical data produced by the

KCEL will be maintained on its LIMS database in perpetuity. PCB and PBDE congener data produced by AXYS Analytical Services will be loaded onto KCEL data servers. A Microsoft Access database and Excel spreadsheet software will be used to store and tabulate electronic data deliverables. An interim data report will be produced for EPA and the project advisory team.

7.4 Assessments and Response Actions

Data will be reviewed as it is reported by the analytical laboratory to allow for review and potential corrective actions. The primary adaptive response is anticipated to be adjusting the autosampler trigger heights used in the CSO or stormwater pipes. Because flow monitoring and modeling is unavailable for the chosen sampling points, best professional judgment will be used to set trigger heights. As the project progresses and various size storm intensities are observed relative to pipe volumes/heights, trigger points will be revised to capture different size storms.

If review of chemistry data suggests sampling or method revisions outside of those allowed in the cited methods and SOPs are required, an addendum to this QAPP will be prepared.

8.0. PROJECT RESPONSIBILITIES

Project Manager (Jenée Colton) – Coordinates with King County Lab for sampling and conventionals analysis, defines scope and establishes contract with analytical laboratory for PCB and PBDE congener analyses, reviews and edits QAPP, reviews QA package for data usability, reviews data report.

Field Study Technical Lead (Richard Jack) – drafts and finalizes QAPP document, troubleshoots technical problems, approves modifications to sampling methods as needed, ensures sampling and analyses are completed on schedule, writes data report.

Lab Project Manager (Colin Elliott) – coordinates KCEL lab sections for project, ensures all sampling equipment and supplies are prepared and sampling events occur on schedule, reviews and comments on QAPP, ships samples to contract laboratory, and ensures KCEL deadlines are met.

Contract Laboratory (AXYS Analytical Services) – conducts sample analysis for PCB and PBDE congeners, provides data packages

Contract Laboratory Project Manager (Devin Mitchell) – main point of contact for King County, responsible for meeting contract conditions and deadlines.

Contract Laboratory QA Officer (Dale Hoover) – responsible for contract laboratory quality assurance.

QA Officer (Richard Jack) – plans necessary field QC sampling, reviews and approves QAPP, conducts QA validation of all data.

Field Science Unit Supervisor (Ben Budka) – Supervises field staff, schedule and field workload at KCEL, coordinates field sampling project needs with laboratory project manager, ensures staff availability to complete field sampling on schedule. The following individuals are the "field leads" for their respective components of this project:

David Robinson – Downstream Outputs and Lake Washington

Marc Patten – Stormwater, CSOs, and I-90 Bridge Runoff (autosamplers)

Stephanie Hess – Upstream Inputs and Stormwater-Dominated Creeks

Bob Kruger – Atmospheric Deposition

Conventionals Unit Supervisor (Brian Prosch) – supervises all conventional analyses at KCEL, coordinates project needs with laboratory project manager, and ensures conventional analyses are completed on schedule.

Advisory Panel (see members under Distribution List) – Assists in site selection and access permissions, reviews and comments on QAPP, and provides feedback on progress in context of overall project goal.

9.0. PROJECT SCHEDULE

Sampling will occur over a year with initiation estimated in April 2011. The exact sampling day and time will vary depending on sample location and weather conditions. Refer to Table 17 for project activities and timelines.

Table 17. Field Study Project Schedule

Activity	Time period	Staff	Description
Site selection	Dec 2010 - Jan 2011	Jenée Colton, Sally Abella, 2 KCEL staff	Select sampling sites for input pathways, export pathways and Lake Washington
Atmospheric deposition sampler design	January 2011	Jenée Colton, Richard Jack, 2 KCEL staff	Select sampler design for bulk air sampling
Write QAPP	Jan-March 2011	Richard Jack, Jenée Colton	Write draft and final Quality Assurance Project Plan
Finalize contract with AXYS	Feb-March 2011	Jenée Colton	Write and get Scope of Work and contract signed
Atmospheric sampler fabrication	March 2011	2 KCEL staff	Make 2 atmospheric deposition samplers
Organize and setup equipment	Mar - April 2011	2 KCEL staff	Organize and select autosamplers for each location, test batteries, pumps, flow meters, etc.
Conduct field study	April 2011 - April 2012	Jenée Colton, Richard Jack, various KCEL staff	Deploy samplers and collect samples according to QAPP design.
Analyze samples	April 2011 – June 2012	Various KCEL staff, AXYS	Analyze samples for conventional and PCB/PBDE congeners
Validate, analyze and report results	May - July 2012	Jenée Colton, Richard Jack, Deb Lester	Conduct data validation, calculate summary statistics and write Data Report

10.0.INDEX TO QAPP ELEMENTS

EPA QAPP Element	Section(s)	Start page
Group A. Project Management		
A1 Title and Approval Sheet		i
A2 Table of Contents		ii
A3 Distribution List		vi
A4 Project/Task Organization	8.0	60
A5 Problem Definition and Background	1.0	viii
A6 Project/Task Description	1.1	1
A7 Quality Objectives and Criteria	2.0	13
A8 Special Training/Certifications	6.0	58
A9 Documentation and Records	7.2, 7.3	58
Group B. Data Generation and Acquisition		
B1 Sampling Process Design (Experimental Design)	3.0	17
B2 Sampling Methods	3.2	27
B3 Sample Handling and Custody	4.1, 4.2, 4.3	32, 34, 35
B4 Analytical Methods	4.6, 5.0	36, 45
B5 Quality Control	4.7, 4.8, 4.9, 5.0	37, 45
B6 Instrument/Equipment Testing, Inspection, and Maintenance	4.7, 5.4	37, 56
B7 Instrument/Equipment Calibration and Frequency	4.7, 5.4	37, 56
B8 Inspection/Acceptance of Supplies and Consumables	4.5	36
B9 Non-direct Measurements	separate report	
B10 Data Management	7.2, 7.3	58
Group C. Assessment and Oversight		
C1 Assessments and Response Actions	7.4	59
C2 Reports to Management	7.2	58
D. Data Validation and Usability		
D1 Data Review, Verification, and Validation	7.0, 7.1	58
D2 Verification and Validation Methods	7.1	58
D3 Reconciliation with User Requirements	7.1	58

11.0. REFERENCES

APHA 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. American Public Health Association. Washington, D.C.

Brandenberger, J.M., P. Louchouarn, L-J Kuo, E.A. Crecelius, V. Cullinan, G.A. Gill, C. Garland, J. Williamson, and R. Dhammapala. 2010. Control of Toxic Chemicals in Puget Sound, Phase 3: Study of Atmospheric Deposition of Air Toxics to the Surface of Puget Sound. Washington Department of Ecology, Olympia WA. http://www.ecy.wa.gov/pubs/1002012.pdf

CBP, 2007. Chesapeake Bay Basin Toxics Loading and Release Inventory. Chesapeake Bay Program, 410 Severn Avenue, Suite 109, Annapolis, Maryland 21403

Cerco, C.F., M.R. Noel, S.-C. Kim. 2004. Three-dimensional eutrophication model of Lake Washington, Washington State. Prepared for King County Department of Natural Resources and Parks, Seattle, WA. U.S. Army Engineer Research and Development Center, Vicksburg, MS. ERDC/EL RR-04-12. http://el.erdc.usace.army.mil/elpubs/pdf/trel04-12.pdf

Colton, J., D. Lester, and D. Wilson. 2005. Sammamish River Water and Sediment Quality Assessment. King County Water and Land Resources Division, Seattle, WA.

DOH, 2004. Final Report: Evaluation of Contaminants in Fish from Lake Washington, King County, Washington. Washington State Department of Health, Olympia, WA.

Ecology, 2003. Development of Freshwater Sediment Quality Values for use in Washington State: Phase II Report. Washington Department of Ecology, Olympia WA. http://www.ecy.wa.gov/biblio/0309088.html

EPA, 2010. Integrated Risk Information System. PCB assessment. http://www.epa.gov/iris/subst/0294.htm

EPA, 2007a. Survey of New Findings in Scientific Literature Related to Atmospheric Deposition To the Great Waters: Polychlorinated Biphenyls. EPA No. EPA-452/R-07-012. United States Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

EPA, 2007b. Method 1614, Brominated Diphenyl Ethers in Water Soil, Sediment and Tissue by HRGC/HRMS. EAP No. EPA-R-07-005. United States Environmental Protection Agency, Office of Water. Washington, D.C.

EPA, 2003. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS. EPA No. EPA-821-R-00-002. United States Environmental Protection Agency, Office of Water. Washington, D.C.

EPA, 2001. USEPA Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review. United States Environmental Protection Agency. Washington, D.C. Available at: http://www.epa.gov/superfund/programs/clp/download/olcnfg.pdf

EPA, 2004. USEPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Review, EPA-540-R-05-001 United States Environmental Protection Agency. Washington, D.C. Available at: http://www.epa.gov/superfund/programs/clp/guidance.htm#dioxin

Era-Miller, B., R. Jack and J. Colton. 2010. General Characterization of PCBs in South Lake Washington Sediments. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-106. http://www.ecy.wa.gov/pubs/0903106.pdf

Gray, J. R., G. Douglas Glysson, Lisa M. Turcios, and Gregory E. Schwarz. 2000. Comparability of Suspended-Sediment Concentration and Total Suspended Solids Data. Water-Resources Investigations Report 00-4191 http://water.usgs.gov/osw/pubs/WRIR00-4191.pdf

Gries, T. and J. Sloan. 2009. Contaminant Loading to the Lower Duwamish Waterway from Suspended Sediment in the Green River. Washington State Department of Ecology, Olympia, WA. Publication No.09-03-028 http://www.ecy.wa.gov/pubs/0903028.pdf

Kerwin, J. 2001. Salmon and Steelhead Habitat Limiting Factors Report for the Cedar-Sammamish Basin (Water Resource Inventory Area 8). Washington Conversation Commission, Olympia, WA.

King County. 2005. Highway 520 Bridge Stormwater Runoff Study. By Dean Wilson King County Water and Land Resources Division, Seattle, WA.

King County. 2010. Major Lakes Fish Tissue Monitoring – Sampling and Analysis Plan. Prepared by Jenée Colton and Richard Jack, King County Water and Land Resources Division. Seattle, Washington.

King County. 2011. Real time water quality buoy profiling. http://green.kingcounty.gov/lake-buoy/default.aspx

Lee, S., 2009. In-person communication with Jenée Colton and Richard Jack on December 23, 2009. Sinang Lee, Water Cleanup Coordinator, Department of Ecology, Northwest Regional Office, Bellevue, WA.

Leon, D.B. and J. Lowe. 2009. Washington Department of Ecology Standard Operating Procedure for Automatic Sampling for Stormwater Monitoring V1.0. Accessed 2/4/2011 at: http://www.ecy.wa.gov/programs/wq/stormwater/municipal/SOPAutomatedSampling.pdf

Moshenberg, K.L. 2004. A Sediment Triad Analysis of Lakes Sammamish, Washington, and Union. King County Water and Land Resources Division, Seattle, WA.

Pelletier, G. and T. Mohamedali. 2009. Control of Toxic Chemicals in Puget Sound: Phase 2, Development of simple numerical models: The long-term fate and bioaccumulation of polychlorinated biphenyls in Puget Sound. Washington Department of Ecology. Olympia, WA. Pub. No. 09-03-015. http://www.ecy.wa.gov/biblio/0903015.html

RCW 70.76. Revised Code of Washington accessed 1/31/2011. http://apps.leg.wa.gov/rcw/default.aspx?cite=70.76

Seiders, K., C. Deligeannis and P. Sandvik, 2007. Washington State Toxics Monitoring Program: Contaminants in Fish Tissue from Freshwater Environments in 2004 and 2005. Environmental Assessment Program, Washington Department of Ecology. Olympia, WA. Pub. No. 07-030-024. http://www.ecy.wa.gov/biblio/0703024.html

Sandvik, P. 2010. Washington State Toxics Monitoring Program: Trend Monitoring for Chlorinated Pesticides, PCBs, PAHs, and PBDEs in Washington Rivers and Lakes, 2008. Environmental Assessment Program, Washington Department of Ecology. Olympia, WA. Pub. No. 10-03-027. http://www.ecy.wa.gov/biblio/1003027.html

Shapiro, J. 1960. The cause of a metalimnetic minimum of dissolved oxygen. Limnology and Oceanography. 5(2):216-227.

Siddiqi, M.A., R.H. Laessig, K.D. Reed. 2003. Polybrominated diphenyl ethers (PBDEs): New Pollutants – Old Diseases. Clinical Medicine and Research. 4(1):281-290.

Smith, S.L., D.D. MacDonald, K.A. Keenleyside, C.G. Ingersoll, L.J. Field. 1996. A Preliminary Evaluation of Sediment Quality Assessment Values for Freshwater Ecosystems. J. Great Lakes Res. 22(3):624-638.

Tetratech and Parametrix, 2003. Lake Washington Existing Condition Report. Sammamish/Washington Analysis and Monitoring Program. King County Water and Land Resources Division. Seattle, Washington.

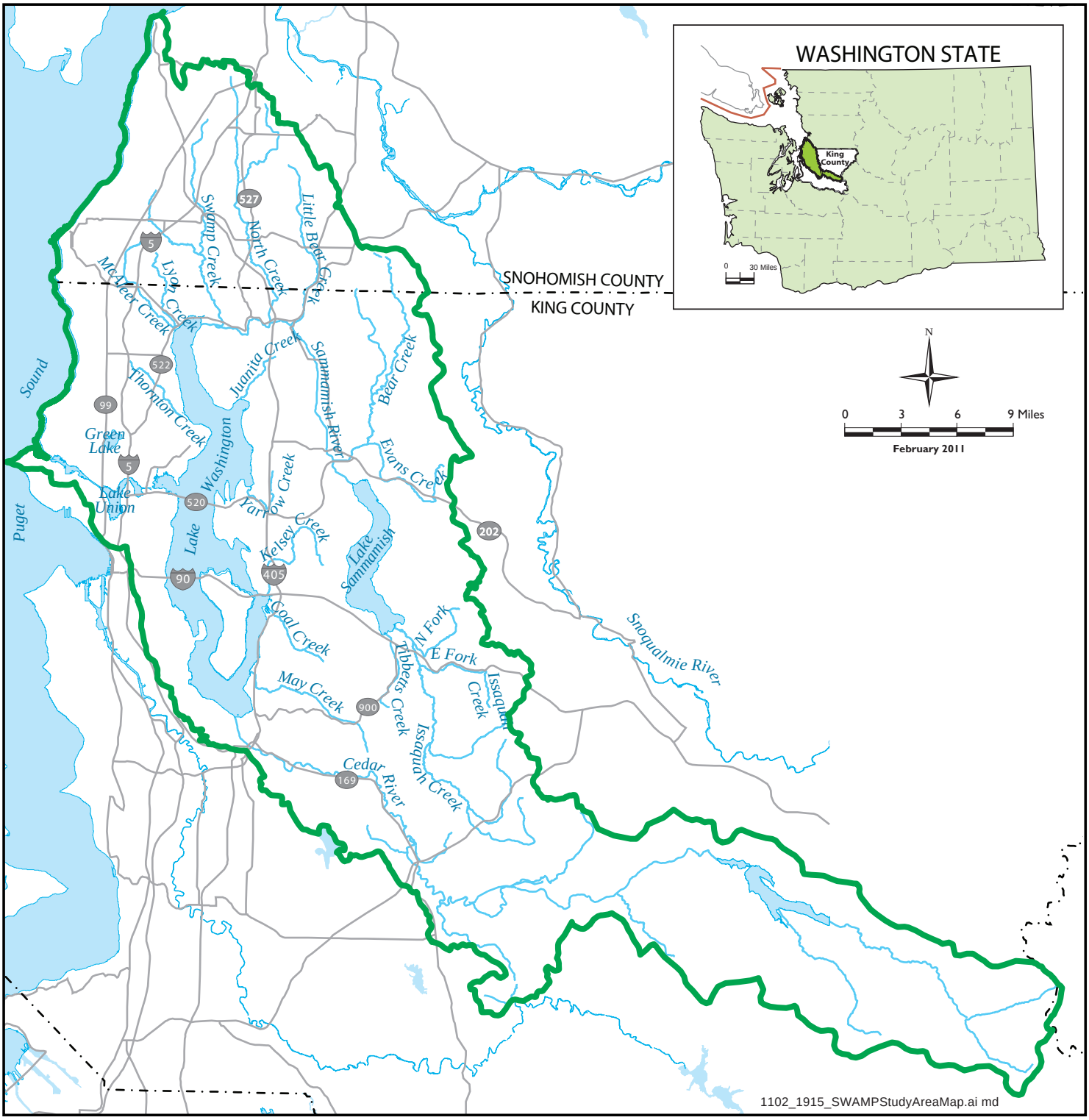


Figure 1

Greater Lake Washington Watershed

- Streams
- Major Roads
- Watershed Boundary
- Lakes

King County

Department of
Natural Resources and Parks
Water and Land Resources Division

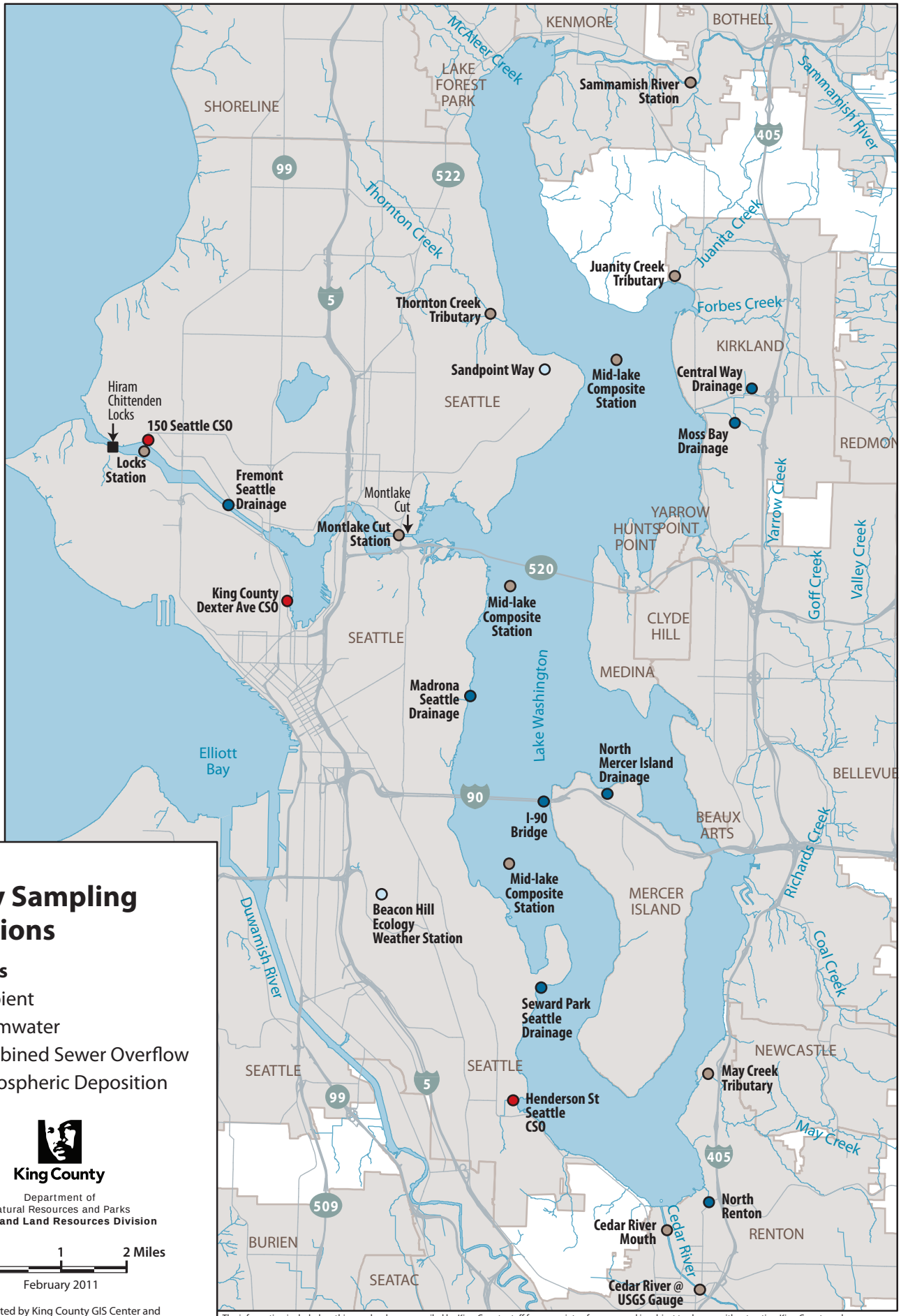


Figure 7

Study Sampling Locations

Stations

- Ambient
- Stormwater
- Combined Sewer Overflow
- Atmospheric Deposition

King County

Department of
Natural Resources and Parks
Water and Land Resources Division

0 1 2 Miles

February 2011

Map created by King County GIS Center and DNRP GIS/Visual Communications/Web Unit.
Data King County Datasets
File 1102epaLKwaSAMPlocMAP.ai wgab

The information included on this map has been compiled by King County staff from a variety of sources and is subject to change without notice. King County makes no representations or warranties, express or implied, as to accuracy, completeness, timeliness, or rights to the use of such information. This document is not intended for use as a survey product. King County shall not be liable for any general, special, indirect, incidental, or consequential damages including, but not limited to, lost revenues or lost profits resulting from the use or misuse of the information contained on this map. Any sale of this map or information on this map is prohibited except by written permission of King County.

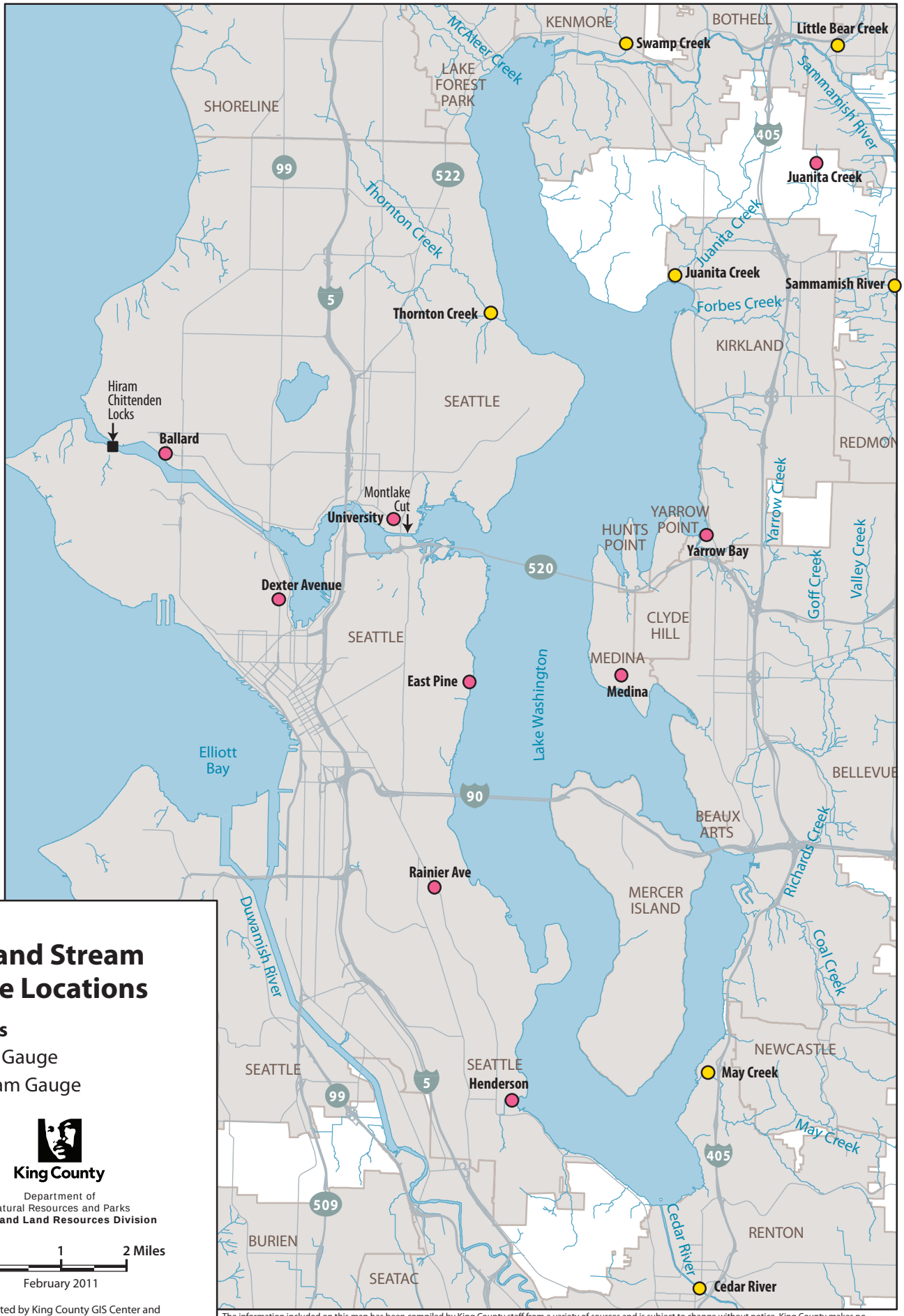


Figure 8

Rain and Stream Gauge Locations

Stations

- Rain Gauge
- Stream Gauge

King County

Department of
Natural Resources and Parks
Water and Land Resources Division

0 1 2 Miles

February 2011

Map created by King County GIS Center and
DNRP GIS/Visual Communications/Web Unit.
Data King County Datasets
File 11102rainGageLOC.ai mdev

The information included on this map has been compiled by King County staff from a variety of sources and is subject to change without notice. King County makes no representations or warranties, express or implied, as to accuracy, completeness, timeliness, or rights to the use of such information. This document is not intended for use as a survey product. King County shall not be liable for any general, special, indirect, incidental, or consequential damages including, but not limited to, lost revenues or lost profits resulting from the use or misuse of the information contained on this map. Any sale of this map or information on this map is prohibited except by written permission of King County.

Appendix A

Bulk deposition sampler design

For EPA Agreement PC-00J28501-0
King County Atmospheric Deposition Sampler Specifications
2/4/2011

Atmospheric deposition samplers for this study are intended to collect rainwater and particulates that fall into the collection basin. These data will be used to estimate loadings of PCBs and PBDEs from atmospheric deposition. This sampler design is a modification of the design used by Pacific Northwest National Laboratories (PNNL) (Brandenberger et al. 2010). The sampler design was modified for multiple reasons: to adapt to the parameters targeted, to avoid field extraction with solid phase extraction (SPEs) discs which was shown to have poor extraction efficiency for PBDEs based on QC sample results, and to make small improvements based on King County field sampling experience during the Puget Sound PNNL study. Samples will be collected by King County staff and analyzed for PCB and PBDE congeners by AXYS Analytical Services in British Columbia, Canada.

A sample and sample replicate sampler will be constructed side-by-side on the same structure. Rainwater and air particulates will be collected using a 14”-20” diameter stainless steel basin. The basin will have a welded stainless tube. Using Silicon/Vinyl pump tubing, a length of 3/8” to ½” ID Teflon ® tubing attaches to the stainless tube. The Teflon ® tubing will lead to a collection vessel. The collection vessel will be a four-liter amber, glass bottle. The collection vessel will have a cleaned Teflon ® coated lid through which the Teflon ® tubing will be led. The lid will also have a second piece of Teflon ® tubing that leads out and hangs downward to prevent a vacuum from forming. Wet deposition will collect in the pan/funnel and drain into the glass collection vessel. Dry deposition will collect on the pan/funnel and be brushed and rinsed into the collection vessel using a natural bristle brush and deionized water from a Teflon ® rinse bottle. Following rinsing and cleaning of the pan/funnel and tubing, the collection vessel will be capped, placed into an ice chest to be kept at 4 degrees C and transported to the King County Environmental Laboratory for storage and transfer to AXYS Analytical Services.

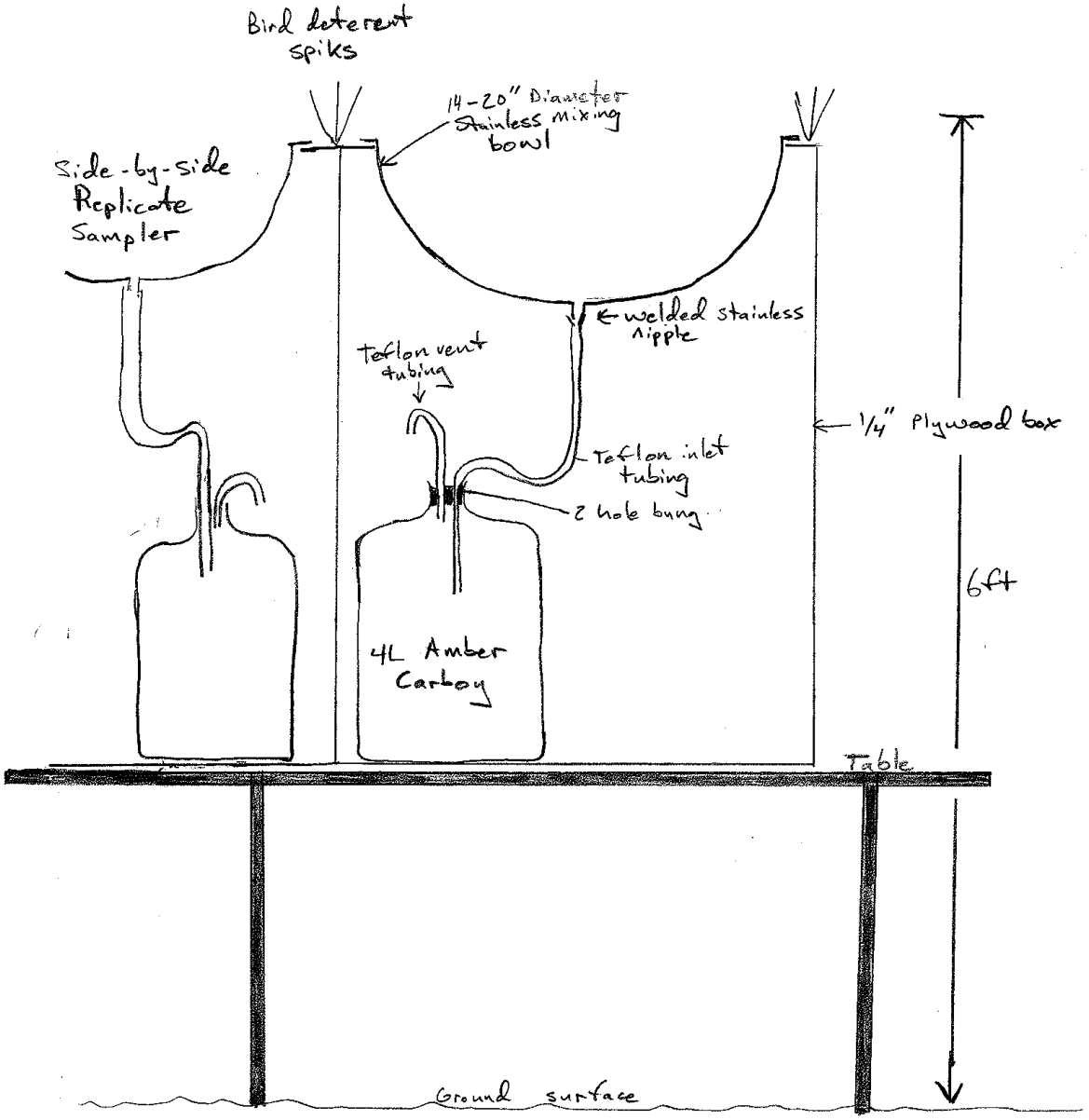
The pan/funnel will be attached to the top of a wooden structure and sit approximately 6 feet off the ground. The glass collection bottle will be contained inside the wooden structure to shield the wet deposition sample from light exposure to prevent photo-oxidation. The wooden structure will be built of plywood and 2x2 beams. Teflon, wood or stainless bird-repellant “skewers” will be placed around the edge of the pan/funnel. Weights will be used to keep the entire structure from sustaining wind damage.

The basin will be decontaminated using 1) Alconox or other suitable laboratory detergent, 2) a DI water rinse, 3) a hexane rinse and 4) an acetone rinse. The Teflon ® tubing, and natural bristle brush will receive this same cleaning protocol although hexane will not be used in silicon tubing to prevent chemical damage. The 4 liter glass collection vessel will be pre-cleaned by AXYS Analytical Services using their proofed PCB congener cleaning protocol.

Below is a schematic of the sampler design.

King County
Department of
Natural Resources and Parks
Water and Land Resources Division
201 South Jackson Street, Suite 600
Seattle, WA 98104

Bulk Deposition Sampler
Not to Scale
Profile view



References:

Brandenberger, J.M., P. Louchouarn, L-J Kuo, E.A. Crecelius, V. Cullinan, G.A. Gill, C. Garland, J. Williamson, and R. Dhammapala. 2010. Control of Toxic Chemicals in Puget Sound, Phase 3: Study of Atmospheric Deposition of Air Toxics to the Surface of Puget Sound. Prepared by the Pacific Northwest National Laboratory for the Air Quality Program, Washington Department of Ecology, Lacey, WA. www.ecy.wa.gov/pubs/1002012.pdf

Appendix B
Autosampler SOP

Washington State Department of Ecology

Standard Operating Procedure for Automatic Sampling for Stormwater Monitoring

Version 1.0

Authors: Dana B. de Leon, City of Tacoma
Julie Lowe, Washington State Department of Ecology

Reviewers: Rick Fuller, City of Tacoma
Dylan Ahearn, Herrera Environmental Consultants, Inc.
Kurt Marx, Taylor Associates, Inc.
Bill Taylor, Taylor Associates, Inc.
Doug Hutchinson, City of Seattle
Stormwater and Watershed Program Staff, Washington State Department of Transportation
Bob Hutton, Clark County

QA Approval - William R. Kammin, Ecology Quality Assurance Officer
Date – 9/16/2009

ECY002

SIGNATURES ON FILE

Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process. Any deviation for the SOP should be documented.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)

1.0 Purpose and Scope

1.1 This document is the Department of Ecology's Standard Operating Procedure (SOP) for collection of stormwater samples using automated equipment. This SOP is designed to be used for in-pipe stormwater discharge sampling and covers a variety of technologies. Most but not all steps may also be used for open channel installations.

1.2 This SOP applies to those activities that involve the programmable automated collection of composite water quality samples. The purpose of this SOP is to provide general guidelines and procedures on how automatic samplers work, how to install and program the instruments, and sample collection and processing procedures.

1.3 This SOP describes programming and collection procedures when using automated samplers, (in common terms) for both flow-weighted and time-weighted sampling and base flow compositing.

2.0 Applicability

2.1 Storm runoff and base flow are collected and transported through natural channels, ditches, culverts and engineered pipe and treatment systems. Each monitoring site will have individual characteristics that require a specific configuration of equipment and installation that best enables the collection of representative water quality samples. A successful location for automatic samplers features stable hydraulics and the ability to install sampling equipment. Other important factors include selection of a water quality monitoring site representative of a specific land use or activity, and if calculating pollutant loadings, selecting a location that provides accurate (as defined in the project QAPP) determination of flow (water quantity) in addition to water quality.

2.2 When sampling runoff or BMP influent/effluent, care must be taken to obtain samples from points that are not affected by pre-water quality treatment.

2.3 Additionally, groundwater, back water conditions or tidal influences and interactions should be avoided in the stormwater sample and may require further modification of these procedures.

2.4 Automatic samplers can be configured to collect composite samples to reflect a mean water quality concentration. Composite sampler configurations can include:

2.4.1 Constant Time/Volume Proportional to Flow Rate or Flow Increment.

2.4.2 Constant Time/Volume Proportional to Flow Volume Increment.

2.4.3 Constant Time/Constant Volume (EPA, 1992).

2.5 Automatic samplers may not represent the complete range of particle sizes in water. Automatic samplers are not capable of sampling bed load material and are less effective in sampling larger particles. They can be effective in representing particles up to about 250 µm if the sampler intake is suitably located to collect subsamples from a well-mixed sample, such as from a cascading stream (SSFL, 2008).

2.6 Bed load samples and special floatable capture nets may be needed to supplement automatic samplers if information for the complete range of solids is needed (SSFL, 2008).

3.0 Definitions

3.1 **Automated Sampler**: A portable unit that can be programmed to collect discrete sequential samples, time-composite samples or flow-composite samples (WCD, 2007).

3.2 **Base flow**: flows occurring in the drainage after 48 hours with no measurable rainfall or less than 0.02 inches (City of Tacoma).

3.3 **Best Management Practice (BMP):** Physical, structural, and/or managerial practices that, when used singly or in combination, reduce the downstream quality and quantity impacts of stormwater (National Research Council, 2008).

3.4 **Composite Sample**: Used to determine "average" loadings or concentrations of pollutants, such samples are collected at specified intervals, and pooled into one large sample, can be developed on time, flow volume or flow rate. Four types of composite samples can include:

3.4.1 **Constant Time/Volume Proportional to Flow Rate**: Samples are taken at equal increments of time and are composited proportional to the flow rate at the time each sample was taken (Appendix A, Figure 1). This type of composite sample would typically require manual compositing of sub-samples taken from each time-series aliquot (collected manually or by auto sampler) based on a flow meter record , and require using only the instantaneous flow rate at the time each aliquot was collected (a spreadsheet is needed to do this). A fully-automatic flow weighted composite sample of this type is not typically used or even possible with an auto-sampler/flowmeter. This is also commonly referred to as a flow weighted composite sample.

3.4.2 **Constant Volume/Constant Flow Volume Increment**: Samples of equal volume are taken at equal increments of flow volume and composited (Appendix A, Figure 2). This type of composite sample is most often used and can be completely automated using conventional auto sampler and flow meter pairs, and does not require manual compositing of sub-sample aliquots unless for other special purposes, such as a paired set of time-series samples to complement the composite sample. This is also commonly referred to as a flow proportional composite sample.

3.4.3 **Constant Time/Volume Proportional to Flow Volume Increment**: Samples are taken at equal increments of time and are composited proportional to the volume of flow since the last sample was taken (Appendix A, Figure 1). This type of composite sample would typically require manual compositing of sub samples from time-series aliquots (collected manually or by auto sampler) based on a flow meter record, and require totaling the flow volume increments between sampling (a spreadsheet is needed to do this). A fully-automatic flow weighted composite sample of this type is not typically used or even possible with an auto-sampler/flow meter. This is also commonly referred to as manual flow proportional compositing.

3.4.4 **Constant Time/Constant Volume**: Samples of equal volume are taken at equal increments of time and composited to make time-composite an average sample. This method is the simplest and does not require flow measurement, but it does not yield a flow-weighted composite. This type of method may be well suited for certain special studies including toxicity assessments. However, this method is not consistent with the current stormwater permit application regulations (EPA, 1992) (Appendix A, Figure 4). This is also known as a time composite sample.

3.5 **Confined Space Entry Site** – A space that is large enough and so configured that an employee can bodily enter and perform assigned work, has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry) and is not designed for continuous employee occupancy (OSHA, 2009).

3.6 **Conveyance System**: A single pipe or series of pipes that convey stormwater as part of a municipal separate storm sewer drainage system (EPA, 2008).

3.7 **Drainage Area**: The area contributing runoff to a single point measured in a horizontal plane, which is enclosed by a ridge line (National Research Council, 2008).

3.8 **Event Mean Concentration (EMC):** Pollutant concentration of a composite of multiple samples (aliquots) collected during the course of a storm. The EMC accurately depicts pollutant levels from a site and is most representative of average pollutant concentrations over an entire runoff event (SSFL, 2008).

3.9 **Event Mass Load (EML):** calculated by multiplying event mean concentration (EMC) by event runoff volume.

3.10 **Hydrograph**: A graph of runoff rate, inflow rate or discharge rate past a specific point as a function of time (National Research Council, 2008).

3.11 **Hyetograph**: A graph of measured precipitation depth (or intensity) at a precipitation gauge as a function of time (National Research Council, 2008).

3.12 **Mean Concentration (MC)**: either the arithmetic mean or the flow-weighted mean of instantaneous concentrations for a pollutant parameter. Flow-weighted mean is the flow-rate weighted average of instantaneous concentrations corresponding to the measured runoff flow rates (Stormwater, 1995).

3.13 **Outfall**: Point source where an effluent or municipal separated storm sewer system discharges into receiving waters (EPA, 1992, Ecology, 2009).

3.14 **Pollutant Load**: A mass concentration multiplied by the total volume of water passing by a certain point in time.

3.15 **Stormwater**: That portion of precipitation that does not naturally percolate into the ground or evaporate, but flows via overland flow, interflow, channels or pipes into a defined surface water channel or a constructed infiltration facility. According to 40 CFR, part 122.26(b)(13), this includes stormwater runoff, snow melt runoff and surface runoff and drainage (National Research Council, 2008).

3.16 **Time of Concentration**: The time of travel for rain runoff from the farthest point in the tributary area to the sampling location.

4.0 Personnel Qualifications/Responsibilities

4.1 All field staff will be familiar with other standard operating procedures for water quality sampling and/or trained to collect representative environmental samples. This practice will ensure that the sampling event is completed efficiently and cross-training on all aspects of sampling will have been completed. Staff must demonstrate a competency for sample collection using appropriate sampling equipment and techniques.

4.2 The field lead directing sample collection must be knowledgeable of all aspects of the project's Quality Assurance Project Plan (QAPP) and/or project goals and objectives to ensure that credible and useable data are collected.

4.3 All field staff will have OSHA's 8-Hour Confined Space Entry certification if confined space entry is required to access the sampling location, perform maintenance and/or sample collection.

4.4 Other training requirements may be necessary depending on situations encountered at each site.

5.0 Equipment, Reagents, and Supplies

5.1 Automated sampler.

5.2 Flow rate recording equipment is highly recommended to be installed with flow monitoring equipment.

5.3 Portable computer or data transfer unit.

5.4 Automatic sampler unit's bottle configuration section.

5.5 Pre-cleaned Suction intake tubing (Teflon® or Teflon®-lined) and hose clamps.

5.5.1 For the suction intake tubing, Teflon® or Teflon®-lined tubing is required if organic analysis because of its inert properties. Polyethylene is acceptable for non-organic analysis, however silicone-rubber tubing is used through a peristaltic pump. To determine the length of tubing needed, see Section 6.3.1.

5.6 Mounting ring for holding tubing within a piped system.

5.7 Anchors or anchoring system (stainless steel plate or bands) to secure tubing in place.

5.8 Stainless steel inlet strainer.

5.9 Power source (deep cycle RV/Marine battery, rechargeable battery, AC power source or solar-powered batteries) and connector cables.

5.10 Water quality instrument and probe (pH/conductivity/temperature meter and probe).

5.11 Triggering equipment (liquid level actuators are sometimes used for flow-proportional composite sampling as a trigger for sample collection.

5.12 Miscellaneous tools (knife, scissors, flat-head and Phillips screwdrivers, portable battery-powered drill and drill bits, a measuring tape, rope, duct tape, ty-raps and diagonal cutter, survey tape, fluorescent spray paint, and extra batteries for instruments).

5.13 Safety and personal protective equipment (flashlights and head lamps, dry chemical hand-warmer heat packs, hand sanitizer, hart hats, safety glasses/goggles, disposable gloves, earplugs, first aid kit, traffic safety cones, and high visibility safety clothing).

5.14 Site access tools (shovel and brush removal tools, manhole hook and sledge hammer, waterproof boots and waders).

5.15 Documentation/field recording equipment (writing instruments, clip board, *Rite-in Rain*™ field sheets/notebook, laboratory Chain-of-Custody (COC) forms).

5.16 Decontamination and sample processing equipment (de-ionized water, large plastic bags, ice and plastic barrier, clean, non-metallic ice chest, corn or churn splitters, decontaminated sample bottles either Teflon®, glass or polyethylene but based on parameters to be sampled).

5.17 Confined Space Entry Equipment, if applicable, portable multi-gas meter, full body harness, ventilating blower and power source, 3-way rescue and recovery tripod and winch system. Other materials needed for confined space entry as specified in OSHA Occupational Safety and Health Standards 1910.146 and Washington Administrative Code 296-809.

6.0 Summary of Procedure

6.1 Monitoring Site Selection

6.1.1 Select a representative site to ensure data is collected which best represents the storm runoff condition through the stormwater conveyance.

6.1.2 A representative sampling location should include a stormwater outfall location where stormwater is relatively well mixed and relatively “stable” or “uniform”. For selecting sites with uniform flows, avoid steep slopes, junctions, confluences, grade changes, and areas of irregular channel shape due to breaks, repairs, roots, debris, etc. Sites with pipe slopes less than 2% typically have uniform flows.

6.1.3 Select sites where the channel and storm drains are soundly constructed and have free-flowing (gravity flow) conditions.

6.1.4 Avoid selecting sites affected by backwater and/or tidal conditions since these areas can complicate measurement of flow and the interpretation of data.

6.1.5 For selecting BMP sites, determine the total number of inlets and outlets. If more than one, additional samplers may be needed to characterize multiple inlets/outlets.

6.1.6 Ensure the influent sampling station will not include any prior treatment of stormwater upgradient from the station.

6.1.7 Obtain permission (if applicable) for site access (Ecology, 2007) and conduct a follow-up site inspection during dry and wet weather.

6.1.8 Note the following information for each selected monitoring site in field notebooks:

6.1.8.1 The contributing drainage area flowing to the site.

6.1.8.2 The discharge tributary system (discharge to receiving water or other area).

6.1.8.3 Site constraints or safety concerns .

6.1.9 Dry and Wet Weather Inspections.

6.1.9.1 During dry weather, inspect the site for base flows (dry weather flows, presence of debris, signs of staining, odors, discoloration in water, unusual flows and/or excessive sediment deposits. Note observations in field notebooks.

6.1.9.2 During wet weather, inspect the discharge flow condition to get a sense for sampling conditions during storm runoff events. Note observations in field notebooks.

6.2 Delineating the Drainage Area to the Monitoring Site

6.2.1 Delineate the drainage area by determining which areas drain to the monitoring location. The delineation will help identify potential sources from land uses/contributing area, estimate the time of concentration and establish jurisdictional authority. This will likely be an important part of identifying stakeholders in the watershed or sub-basin (Ecology, 2007).

6.2.2 Obtain drainage system information from the local jurisdiction (piping and/or stormwater conveyance system, source maps, GIS files and Auto Cad files).

6.2.3 For delineating your drainage area, surface water drainage from the landscape typically follows topography in most areas, with a common exception being urban areas (Ecology 2007). However, in some instances, stormwater conveyance systems are designed to pump up hill to tie into drain pipes.

6.3 Equipment Installation

6.3.1 For installation of the suction tubing intake, meter probes and triggering equipment, locate the appropriate place at the monitoring station for representative placement. The selected area should be an area where the runoff stream is adequately well mixed to ensure representative sampling from the entire cross section of the conveyance system (typically mid stream in the pipe/channel). The suction tubing intake, other parameter probes and sampler triggering devices must be placed downstream of flow monitoring devices in such a matter as to not create turbulence which can influence flow measurements.

6.3.2 Prior to installation and equipment handling, wear clean, powder free gloves and practice clean handling techniques.

6.3.3 Cover the end of the suction intake tubing with new aluminum foil, tape or laboratory grade cellophane to prevent contamination during installation.

6.3.4 If confined space entry is required to install the suction intake, insure field staff is properly trained and certified.

6.3.5 Place the intake tubing in the stormwater conveyance system where it will best represent runoff through the system providing at least 2” of depth or greater for the intake. The suction intake must be covered during sampling to avoid improper aliquot collection.

6.3.6 For placement of the suction intake in less than 2 inches of water, a depth can be created by constructing a deeper pool using sandbags, weirs or flumes.

6.3.7 Take caution when placing any constriction in the pipe since it can also cause sedimentation which can cover the intake and affect the aliquot volume collected.

6.3.8 If constricting items are used, provide regular maintenance and checks to keep the sampler intake free of debris and sedimentation.

6.3.9 If necessary, mount the suction intake slightly above mid stream on one side of the pipe/channel if high solids loadings (bed load, trash, debris) are present. However, with the suction intake offset of the mid channel, low flows may not completely submerge the strainer.

6.3.10 Place the suction tubing mid stream, facing upstream, parallel to the water flow and downstream of the flow measuring device. The line should not be placed in an eddy or area of flow disturbance (WCD, 2007).

6.3.11 Place the line to avoid disturbance or turbulence in the flow pattern (this could interfere with flow measurements).

6.3.12 Prevent clogging by adjusting the tubing at an angle.

6.3.13 Use an anchor system or anchors to secure the tubing. Some manufacturers have a mounting plate available to mount the tubing and other probes in the channel or pipe.

6.3.14 Anchor the line to prevent bending/crimping during high velocity storm flows within the pipe/channel. Place an anchor every 20 inches for higher-velocity flows.

6.3.15 Ensure there are not kinks or dips in the tubing which can hold residual amounts of liquid or deposited sediments that could cross-contaminate sample volumes (WCD, 2007).

6.3.16 Attach a strainer to the end of the pre-clean suction intake tubing. Slide the end of the strainer into the tubing and secure it with a stainless steel hose clamp.

6.3.17 Cut the tubing to the desired length in 1 foot increments and cap the end with new aluminum foil, tape or laboratory grade cellophane to prevent contamination.

6.3.17.1 The minimum length of the pump tubing must be used to minimize the contact of the sample water and tubing as the sample water is carried from the intake tubing into the sample containers. See the manufacturer documentation on the technical limits for the automatic sampler pump and the recommended maximum length of tubing, and for limitations in elevation difference between pickup point and sampler.

6.3.17.2 If the sampling program is long-term, the suction intake tubing can remain in-place for extended periods, however, provisions must be made for flushing the tubing thoroughly with deionized water before each sampling event and with site water (deionized or ambient water) before each aliquot is drawn. It is recommended to replace the tubing periodically, semiannually or annually, depending on site conditions, project QAPP, and experience with specific tubing. Frequency of replacement and methods used for cleaning of the tubing should be support with collection of quality assurance/quality control (QA/QC) samples.

6.3.18 Measure the entire length of tubing since this information is needed when programming the automated sampler. Record measurements in field notebooks (WCD, 2007).

6.3.19 Install all other appropriate probes and/or sampler triggering device near the suction intake tubing placement.

6.3.20 All equipment installed within the stormwater conveyance systems should be secured in a way to not create turbulence and not to dislodge from the sampling location. Turbulence can create cavitations (air pockets) around the suction intake which varies the volume of water sampled for each aliquot.

6.3.21 For installation of the automated sampler, place the sampler on a level surface as close to the sample intake as possible. See the manufacturer documentation on the technical limits for the automatic sampler pump including vertical pump height and the recommended maximum length of tubing. It is recommended that the vertical distance be a maximum between 26-28 feet depending on equipment used. The sampler should never be placed at a height below the sampler intake. This situation would create a siphon

6.3.22 When sampling for metals, only stainless steel fittings or clamps should be used in all areas of sample contact. Other metallic hardware (plates, fittings, conduit and clamps) should not be used in areas of sample contact. Take care to ensure that the ends of all tubing do not touch any object that is not known to be clean during installation. Metallic hardware can be used only in areas where contact with the sample doesn't occur e.g., anchors used on the outside of the tubing.

6.3.23 For above-ground enclosures, install housing/enclosure for the equipment well above the highest water level expected.

6.3.23.1 Secure enclosure in such a manner to prevent tipping, vandalism, or theft.

6.3.23.2 Use electrical metal conduit, plastic conduit or a water pipe to protect the length of sample intake tubing from sampling point into the enclosure. Make sure the conduit is large enough to accommodate all connection cables (flow meter, parameter probes, rain gauges), and that any rough or sharp edges resulting from cutting the conduit are removed by reaming or scraping.

6.3.23.3 Place the sampler on a level surface within the enclosure and lock to prevent equipment theft/vandalism.

6.3.24 For placement within a manhole or junction box, place the automated sampler either on a shelf in the manhole/catch basin junction box or hang sampler inside the manhole/catch basin. Some manufactures have suspension harnesses and other anchors commercially available.

6.3.24.1 Make sure that the sampler is above any high water level within the pipe. High water, such as surcharging or tidal water, can float the sampler damaging the sampler unit and/or its electronics and can contaminate the enclosed sample container(s) once the sampler is submerged.

6.3.24.2 Secure the sampler in place.

6.3.24.3 Install a secondary "safety line" for all equipment to prevent equipment from being lost if platform or hanger fails.

6.4 Preparing the Sampler

6.4.1 Remove the cover or top of sampler and carefully place it to the side making sure not to kink the sample intake line.

6.4.2 Prepare the base section for the desired configuration (composite bottle or sequential multi-bottle setup).

6.4.3 Place the cover back on and feed the pre-cleaned flexible pump tubing through the peristaltic pump and into the area of the sampler where the sample bottle(s) are housed.

6.4.4 Take care to ensure that the ends of the tubing do not touch any object that is not known to be clean during installation.

6.4.5 Slide the end of the sample intake tubing (at least ½ inch) into the pump tubing and secure it with a hose clamp, if necessary.

6.4.6 Connect other equipment to sampler such as flow meters, rain gauges, level actuator, and/or parameter probes.

6.4.7 Attach power source to sampler (solar, AC, battery).

6.4.8 Turn on sampler and any other equipment.

6.4.9 To check sampler function, purge the sample tubing with site water or de-ionized water to make sure the sampler is operating properly. See manufacturer's manual.

6.5 Flow-Proportional-Sampling

6.5.1 Examples of collecting a flow-proportional composite samples include sampling of the same sample aliquot volume at a predetermined runoff volume interval (e.g., one sample aliquot collected every thousand cubic feet) (i.e., volume proportioned), or collected on an even-time basis with sample aliquot volume proportional to the instantaneous flow rate (i.e., flow proportioned). This method is typically not used automatically since most equipment does not support this function.

6.5.2 Flow-proportional composite samples collect more frequently at higher flow rates and less frequently at lower flow rates (as flow rate increases, the time between aliquots decrease). This method is a direct measure of the storm's hydrograph or the relationship between the pollutant concentration and flow rate. This allows a direct estimation of event mean concentration (EMC) and Event Mass Load (EML).

6.5.3 Key parameters for flow-proportional sampling include:

6.5.3.1 Forecasted precipitation volume/amount.

6.5.3.2 Expected amount of runoff volume.

6.5.3.3 Expected storm duration.

6.5.3.4 Expected peak flow rate.

6.5.3.5 Minimum composite volume required for desired analyses.

6.5.3.6 Minimum accepted number of aliquots, sample aliquot size, and maximum bottle volume.

6.5.4 Sequential (multi-bottle) Sampling:

6.5.4.1 Sequential sampling allows for isolation of specific samples or groups of samples from specific periods of the runoff hydrograph and provides more visual indication of sampler malfunction if it occurs.

6.5.4.2 For sequential sampling, program the sampler on either flow-proportioned or time composite sampling scheme.

6.5.4.3 If each sample is collected on the flow-proportioned or time basis and if each aliquot volume sampled is uniform, the samples can be combined to represent a flow-proportioned or time composite, respectively, of the specific period of interest.

6.5.4.4 If discrete samples are collected on a time or non-uniform flow basis, a flow-proportioned composite sample could be created by splitting each discrete sample in proportion to the discrete sample's runoff volume or instantaneous flow rate at the time of sample collection.

6.5.4.5 Key parameters for sequential sampling include, but are not limited to:

6.5.4.5.1 Minimum composite volume required for desired analyses.

6.5.4.5.2 Minimum accepted number of aliquots and sample aliquot size.

6.6 Time Composite Sampling.

6.6.1 Time composite samples are collected by sampling the flow at a set time intervals (e.g., one sample aliquot collected every ten minutes). The sample aliquot volume is the same for each sample collected.

6.6.2 Key parameters for time composite sampling include:

6.6.2.1 Desired time interval.

6.6.2.2 Minimum composite volume required for desired analyses.

6.6.2.3 Minimum accepted number of aliquots and sample aliquot size.

6.6.2.4 Maximum bottle volume.

6.7 Sampler Programming

6.7.1 Automatic samplers alone or with flow measurement devices can be programmed to collect various types of samples including: time composite, flow composite, and sequential (multi-bottle) sampling schemes. Each type of equipment system has unique programming elements, however, these three elements are common to all systems: flow quantity interval, total number of aliquot samples and the volume of each aliquot sample.

6.7.2 In general, the automated sampler is programmed to collect a sample aliquot each time it receives a pulse. The pulse can be either time-based or flow-based.

6.7.3 For specific, step-by-step procedures for programming the automated sampler, refer to the Manufacturer's User Manual.

6.7.4 Programs can vary between automated equipment but some elements are similar and include: start sampling (enable) and end sampling (disable) options. These options are dependent upon flow depth, flow velocity, precipitation amount, or time.

6.7.5 If tidal influences are present at the monitoring site, program the sampler to pause/disable in the middle of a storm event to avoid sampling marine water.

6.7.6 To ensure collection of representative samples, automatic samplers should be programmed to perform a back-flow purge cycle in between each aliquot collected. Purging the sample intake tube prior to collection of each aliquot also helps keep the line clear.

6.7.7 Programming for Flow-Proportional Composite Sampling.

6.7.7.1 Estimate a storm runoff volume for a specifically targeted storm event.

6.7.7.2 Calculate initial programming elements to produce representative samples for a range of storm events.

6.7.7.3 Pace the sampler to fill the composite bottle(s) at an appropriate level based on the forecasted rainfall depth of the storm.

6.7.7.4 Take caution when using storm forecasts. Inaccuracies may contribute to difficulty planning for the actual size of an incoming storm. As a result, a larger than predicted storm event may fill sample bottles too fast or if smaller than forecasted, the sample bottles may only fill partially resulting in insufficient sample volume for analysis.

6.7.7.5 For estimating storm runoff volumes, develop a rainfall to runoff relationship. If this is not possible and/or data are not available, storm runoff volumes can be estimated using computer models or mathematical equations. See Appendix B for two example methods to estimate rainfall/runoff relationship.

6.7.7.6 Refine initial estimates as actual rainfall and runoff data are collected.

6.7.7.7 For estimating the total sample volume needed from the storm event, refer to each chemical and/or biological test which has a volume requirement. Once the analytical tests are selected, the required volumes for each test plus any required QA/QC analyses are summed to calculate the total volume needed for analyses.

6.7.7.8 Bottle schematics and their volumes vary. Typically, 9.5 L (2.5 Gal) composite jars and 12 (1 L), 8 (2 L), 4 (3.7) bottle kits for sequential sampling are available. These volumes are usually sufficient for general characterization sampling.

6.7.7.9 If a greater sample volume is required, modification to the sampler may be necessary, two samplers can be used at the one location or field staff may have to be present on site to replace filled bottles. This set-may require special equipment programming and it is recommended to contact the equipment manufacturer.

6.7.7.10 Determine your programming parameters (flow quantity interval, total number of aliquot samples and the volume of each aliquot sample) by using your estimated storm runoff volume and the total sample volume. These elements are as follows:

V_r / V_{fi} N V_s / V_a

V_r = total runoff volume
V_{fi} = flow quantity interval
N = number of sample aliquots
V_s = total sample volume
V_a = volume of sample aliquot

(WEF, 1993 and California DOT, 2000) (See example in Section 6.7.7.16)

6.7.7.11 First, define the number of sample aliquots needed to produce a sufficient composite sample volume that represents the runoff for the entire sampling event.

6.7.7.12 For representative sampling, it is recommended that the sample aliquot volume be a minimum of 200 milliliters, at least 10 aliquots are collected, and at least 75 percent of the total event volume is sampled.

6.7.7.13 Equipment constraints must also be considered when programming samplers. For example, if battery power is used, the battery capacity and its drain from pumping up the vertical pump distance, purging, and the volume of each aliquot pumped, limits the number of aliquots that can be pumped during a storm event. Please refer to the manufacturer's literature for pumping limitations based on the battery capacity.

6.7.7.14 Additionally, many samplers need 1-2 minutes to complete a pumping cycle (purge and sample pump). It is important to regulate the flow quantity interval such that the sampler does not have to run continuously (make sure pacing rate exceeds the expected peak flow rate). At least 5 minute intervals between aliquots is recommended to allow for a full pumping cycle and to limit drain on the sampler battery.

6.7.7.15 Most storm events will be smaller or larger than predicted, so it is impossible to always fill the sample bottle(s) each time. It is recommended to use an automatic sampler that can stop sampling when the sample bottle is full to prevent overfilling.

6.7.7.16 Example Equation: V_r / V_{fi} N V_s/V_a

Where,
V_r = total runoff volume
V_{fi} = flow quantity interval
N = number of sample aliquots
V_s = total sample volume
V_a = volume of sample aliquot

(WEF, 1993 and California DOT, 2000)

6.7.7.16.1 Example Scenario 1:
Vs = 10 liters (10,000 milliliters)
V_a = 200 milliliters
N V_s / V_a = 10,000/200 milliliters = 50 sample aliquots
Flow Quantity Interval
Vfi Vr/N

If N = 50 sample aliquots and Vr, the total runoff volume is 120,000 cubic feet

Vfi = 120,000 cubic feet / 50 = 2,400 cubic feet is the desired flow quantity interval

6.7.7.17 Because of the variability of storm events, a margin of safety can be provided by setting the sample pacing that will work for a wide range of storm events. For example, program elements can be set to collect the minimum number of aliquots for the minimum desired rainfall event and the minimum composite volume required for analyses. If the storm event is greater than the minimum storm targeted, there will be sufficient volume available in the composite bottle(s) to collect aliquots for the larger event.

6.7.7.17.1 Example Scenario 2:

The minimum amount of rainfall to be sampled is 0.20 inches with the runoff volume of 120,000 cubic feet (cf). The minimum number of sample aliquots, N = 10, and Vs, total sample volume, required for all the desired analyses is 2.5 liters (2,500 milliliters):

Va = volume of sample aliquot
Va Vs/N = 2,500 milliliters /10 sample aliquots = 250 milliliters
Flow Quantity Interval
Vfi Vr/N
Vfi = 120,000 cubic feet /10 = 12,000 cubic feet is the desired flow quantity interval

If the composite bottle is 9.5 liters, 38 sample aliquots can be collected with the volume of sample aliquot, Va, set at 250 milliliters.

6.8 Refining program parameters

6.8.1 Refine program parameters when actual and estimated runoff differs by a factor of 2 or more.

6.8.2 Seasonal and annual program refinements may be necessary to account for seasonal and annual variation in rainfall that affect resulting runoff from precipitation events. These variations can include rainfall intensity, soil saturation, infiltration rate, and changes in impervious areas.

6.8.3 Modify calculations by revising the runoff coefficient. However, keep in mind that there will be some variability based on the storm and basin conditions. Program refinements include optimizing flow quantity interval.

6.8.4 If the composite sample volume collected was less the minimum required, decrease the sample interval.

6.8.5 If the composite bottle(s) fills before the end of the storm, increase the sample interval.

6.8.6 Divide the actual storm runoff volume by the total number of sample aliquots to determine a new flow quantity interval.

6.9 Programming for Time-Proportional-Sampling

6.9.1 Time composite sampling is done by sampling runoff at a set time intervals (e.g., one sample aliquot collected every ten minutes). The sample aliquot volume is the same for each sample collected.

6.9.2 Key parameters for time composite sampling are as follows:

6.9.2.1 Minimum composite volume required for desired analyses.

6.9.2.2 Maximum bottle volume.

6.9.2.3 Duration of storm or event to be sampled.

6.9.2.4 Desired time interval.

6.9.2.5 Minimum accepted number of aliquots.

6.9.2.6 Sample aliquot size.

6.9.3 To program for time-proportional composites, estimate the duration of the targeted storm event.

6.9.4 Program the sampler to fill the composite bottle(s) at an appropriate rate for the predicted precipitation duration. Take caution that it is very hard to predict storm duration. If the actual duration is larger than predicted, the sample bottle(s) will fill too fast, missing the tail-end of the storm, and the samples will not represent the entire storm event. If the duration results in a smaller than predicted storm, your minimum aliquot collection criteria may not be met which could result in insufficient volumes collected for analysis.

6.9.5 Calculate total sample volume (refer to Section 6.7.7.7).

6.9.6 Estimate the forecasted storm and runoff duration.

6.9.7 Program the sampler to begin sampling as early in runoff event as practical and to continue past the end of the storm event and/or set maximum limit (e.g., 24 hours).

6.9.8 Estimate the site's rainfall to runoff relationship (refer to Section 6.7.7.5, Appendix B). If available, site specific data or a computer model can be used. Appendix B contains two examples for estimating rainfall to runoff relationship.

6.9.9 If rainfall to runoff information is unavailable, estimate the runoff duration from the forecasted storm duration, amount of rainfall, and the longest estimated time of concentration for the tributary area. The National Weather Service and/or the National Oceanic Atmospheric Administration forecasts can provide estimates of storm duration along with the amount of rainfall, usually in three hours and six hours increments.

6.9.10 Typically, the runoff duration at the site is longer than the forecasted rainfall duration. The time of concentration (Tc), for the tributary area provides a measure to ensure the pacing is set to obtain a representative sample and to ascertain if sampling of contributions from the entire basin are represented, (i.e. sampling at or near the Tc may not be representative of the entire basin). See Appendix C for examples for estimating time of concentration.

6.9.11 The minimum time to program the auto sampler is 2 times the time of concentration beyond the forecasted end time of the rain event. Refine your estimated as rainfall and runoff data are collected.

6.9.12 Determine the program parameters.

6.9.12.1 The equipment program elements, time interval, total number of aliquot samples and the volume of each aliquot sample, can be determined from the storm runoff volume and the total sample volume. These elements are as follows:

6.9.12.2 T_r / T_i N V_s / V_a

Where,
T_r = runoff duration
T_i = time interval
N = number of sample aliquots
V_s = total sample volume
V_a = volume of sample aliquot

(WEF, 1993)

6.9.12.3 First, it is important to define a representative sample. A representative sample is defined as an adequate number of sample aliquots collected to produce a sufficient composite sample volume that represents the runoff for the entire sampling event. It is recommended that the sample aliquot volume be a minimum of 200 milliliters, that at least 10 aliquots are collected, for a minimum duration of at least two times the time of concentration for the drainage area.

6.9.12.4 Equipment constraints must also be considered in setting program elements. If battery power is used, the battery capacity drains from pumping, purging, and when filling aliquots which can limit the number of aliquots taken during a storm event. Refer to the manufacturer's literature for pumping limitations based on the battery capacity.

6.9.12.5 In addition, many samplers need 1-2 minutes to complete a pumping cycle (purge and sample pump). It is important to regulate the flow quantity interval such that the sampler does not have to run continuously (make sure pacing rate exceeds the expected peak flow rate). It is recommended to program the sampler at 5 minute intervals between aliquot collection to conserve battery power.

6.9.12.6 Program the sampler to stop sampling when the sample bottle is full to prevent overfilling.

6.9.12.6.1 Example Scenario 1: T_r /T_i N V_s/V_a

V_s = 10 liters (10,000 milliliters).
V_a = 200 milliliters
N V_s/V_a = 10,000/200 milliliters = 50 sample aliquots
Ti Tr/N
N = 50 sample aliquots and,
Tr = 4 hours (240 minutes)

Ti = 240 minutes / 50 = approx 5 minutes is the desired time interval

6.9.12.7 Pace the sampler to include a margin of safety that works for a wide range of storm events. For example, pace the sampler to collect a minimum number of aliquots for the minimum desired rainfall duration and the minimum composite volume required for analyses. If the storm event is longer than the forecasted storm duration, there will be sufficient volume available in the composite bottle(s) to collect aliquots during the longer duration.

6.10 Sampler Enables

6.10.1 Most samplers include an “enable/disable” or “start/stop” function. Enable/disable functions can include, but are not limited to:

6.10.2 Rain gauge: The sampler enables when the first rainfall measurement is taken.

6.10.3 Water level or velocity speed: Enable the sampler when base flows or a set water level occurs. For example, the base flow at a site increases from 0 to 0.3 ft in summer due to commercial irrigation but most storms easily exceed 0.5 ft. Thus, the enable is set to 0.32 ft to prevent false enables and ensures that a true storm is sampled and not the irrigation water. Liquid level actuators are sometimes used to enable for sample collection.

6.10.4 Water quality parameters: A conductivity threshold option that exists either alone or in combination with velocity, this can be used in tidal influenced areas (disable functions such as high conductivity readings and zero or negative velocities).

6.11 Measuring Rainfall

6.11.1 It is recommended to measure rainfall at the study site using a simple tipping bucket rain gauge (Ecology, 2008). Set rainfall measurements at intervals that correlate to the flow measurements such as 5 minute, 15 minute or hourly readings.

6.11.2 As an alternative to having a rain gauge on site, use a rain gauge located within the drainage area, or websites (the National Weather Service and National Oceanic Atmospheric Administration) that contain real time precipitation forecasts. These forecasts can help provide estimates of storm duration along with the amount of rainfall to aid in staff deployment.

6.12 Storm Event Staff Deployment

6.12.1 Field crews should be fully prepared to deploy when a qualifying storm event has been forecasted. Once deployed and on site powder free gloves should be worn and clean techniques practiced.

6.12.2 Upon site arrival, field staff should perform field checks. Check battery levels/power sources, tubing and all other connections to the equipment. Additionally, pump the suction tubing with deionzied water (use at least 3x the total line volume).

6.12.3 Remove the sampler base and carefully place it to the side. Be careful not to kink the sample intake line and do not allow the exposed pump tubing end to contact hands or any other surfaces.

6.12.4 Place clean bottle(s) in the base, keeping lids on the bottles. Label each bottle with station ID and the sequential bottle number.

6.12.5 Add ice to the sampler either in the base or around the bottle(s) making sure that the ice and ice water won't come in contact with sample water, contaminating the sample.

6.12.6 Remove lid(s) and place in a clean plastic, sealable bags. Label the bag with the site location name.

6.12.7 Check sample distributor, place sampler top back on the base ensuring the pump tubing end is secure and in place.

6.12.8 Program the sampler and verify that the sampler is in "sampling mode."

6.12.9 Document all activities in the field notebook.

6.12.10 If for any reason the composite sample bottle(s) need replacement during a sampling event, the field crew should:

6.12.10.1 Pause the automatic sampler program.

6.12.10.2 Wear clean powder free gloves and practice clean sampling techniques.

6.12.10.3 Remove the sampler base. Do not allow the exposed pump tubing end to contact hands or any other surfaces.

6.12.10.4 Place lids on filled or partially filled bottle(s), and remove from sampler base. Replace with clean bottle(s).

6.12.10.5 Continue sampler program and verify that the automatic sampler is in sampling mode.

6.12.10.6 Secure sampler at site.

6.12.10.7 Document bottle(s) replacement activities in the field notebook.

6.13 Sample Retrieval

6.13.1 At the end of the storm event, deploy field staff to retrieve sample bottles.

6.13.2 Upon arrival, inspect all components of the automatic sampling system to make sure samples were properly collected. If any unwarranted conditions are found, note conditions in field notebook.

6.13.3 Check battery levels and/or power source.

6.13.4 Visually inspect the components and tubing for damage and/or clogging.

6.13.5 Download field data from the automatic sampling system, rain gauge and other appropriate equipment.

6.13.6 Wear clean powder free gloves and practice clean sampling techniques.

6.13.7 Remove the sampler base. Do not allow the exposed pump tubing end to contact hands or any other surfaces.

6.13.8 Remove sample bottle(s) or entire sampler base. It is recommended to transport sample bottle(s) to lab in the sampler base/tray or cooler for transport.

6.13.9 Handling the samples carefully, as little as possible, and by as few people as possible in order to minimize the risk of contamination.

6.13.10 Place lids on the samples.

6.13.11 Inspect bottle(s) for any problems and make note in the field notebook. Note any empty bottle(s), low sample volumes [one bottle not as full as other bottle(s) or all are low], cracked or broken bottle(s) and/or if any spillage occurred during sample collection or during bottle(s) removal.

6.13.12 Note physical characteristics of each bottle including sample turbidity and approximate liquid volume.

6.13.13 Add ice around the bottle(s) to keep them cool during transport.

6.13.14 Keep samples in dark and cool during transport.

6.13.15 Place sampler top on the base or a new base.

6.13.16 Purge the sample tubing with deionized water or decontaminate the sampler tubing using a phosphate-free detergent and rinse with deionzed water (remove wastewater properly from the site).

6.13.17 Cover the exposed pump tubing with aluminum foil, tape or laboratory grade cellophane.

6.13.18 Place the cover back on the sampler and secure the sampler in place.

6.13.19 Perform any other necessary decontamination processes, program the sampler (if applicable), finish maintenance checks etc. prior to leaving the site.

6.13.20 Secure the sampler at site.

6.13.21 Immediately transport bottle(s) to sample preparation area and/or laboratory.

6.14 Sample Representativeness Evaluation

6.14.1 Create a checklist including the project-specific criteria to evaluate whether or not samples meet appropriate storm event criteria.

6.14.2 As suggested in Ecology Publication No. 07-03-006, *Characterizing Stormwater for Total Maximum Daily Load Studies: A Review of Current Approaches*, February 2007, “representative” storm criteria can include:

6.14.2.1 Volume: No fixed maximum, 0.1 inch minimum and typical range is 0.2 to 0.75 inch.

6.14.2.3 Duration: Typical range is 6 to 24 hours.

6.14.2.4 Antecedent Dry Period: 24 hours minimum.

6.14.2.5 Inter-event Dry Period: 6 hours.

6.14.2.6 Percent of the storm captured (it is recommended that at least 75% of the storm event hydrograph is captured to best represent the storm).

6.14.3 Additional criteria is also needed including: Total precipitation of storm, entire storm event duration.

6.14.4 For sequential sample composting (taking multiple bottles and combining into one representative sample, the following two items must be determined:

6.14.4.1 Percent of the sampling event flow represented by each individual bottle.

6.14.4.2 Which of the sample bottle(s), if any, will limit the compositing of samples. For the most part, aliquots which represent a specified volume collected at a specified flow volume, are collected uniformly throughout the sampling event.

6.14.4.3 From the downloaded rainfall and sampler data, review rainfall hyetograph, runoff hydrograph, time aliquot was collected, and sampler program report.

6.14.4.4 Compare data to acceptable storm capture parameters, such as number of aliquots, percent storm captured, total precipitation of storm.

6.14.5 Make decision whether or not to analyze the sample based on qualification.

6.14.6 In cases where sample bottles have unequal sample volumes, the individual sample(s) should be composited in relative proportion. In such cases, multiple composite samples should be combined using the following equation:

$$\frac{V_n}{V_t} = P_n \quad \text{and} \quad S_t \cdot P_n = S_n \quad \text{or} \quad S_n = S_t \cdot \frac{V_n}{V_t}$$

V_n – volume of flow that passed during the collection of bottle n
V_t – total volume of flow passed during the sample collection event
P_n – percent of the total sampled flow represented by bottles n
S_t – the total volume of sample collected in all bottles combined
S_n – volume of sample contributed from bottle n toward the composite sample

6.14.7 Use appropriate sample handling techniques to minimize exposure of the samples to human, atmospheric and other potential source of contamination.

6.14.8 Use a mechanical splitter or vigorously agitate to ensure that all liquid and solid will be transferred from the sample bottle to the composite bottle.

6.15 Sample Processing

6.15.1 If the samplers are using sequential (multi-bottle) sampling, they will need to be composited to produce a single composite sample. In addition, the composite sample may need to be split into multiple containers for each analysis.

6.15.2 For processing samples, mix samples thoroughly before splitting.

6.15.3 Composite samples may be split into separate bottles by manual vigorous agitation, using a mechanical splitter such as Teflon cone Dekaport splitter or Teflon churn splitter. Consider the following limitations for these methods:

6.15.4 Splitting the composite sample with an additional step using another equipment exposes the sample to another surface which may increase the possibility of contamination.

6.15.5 If you are handling a large volume (5+ gallons), you need to properly agitate it and split into analytical bottles. It is recommended to use a mechanical splitter (Teflon cone Dekaport splitter) to ensure that the samples are split evenly into the composite bottles. This should minimize any bias that could occur when trying to agitate and pour off a certain amount of each subsample into a composite. However, this process can be time consuming, is not straightforward, and may require expensive equipment (eg. $5000 Teflon churn splitter).

6.15.6 If it is difficult to pour from a wide mouth composite bottle into a small analyte bottle you must do it carefully (slowly) which will allow settling. A mechanical splitter (Teflon churn splitter) may be used to continuously agitate a sample and split off the individual analyte bottles.

6.15.7 The preferred method of splitting should balance minimizing bias from splitting the sample and minimizing contamination from sample handling when using a mechanical splitter. The preferred method should be identified in the project specific QAPP.

6.16 Field Calibration and Maintenance

6.16.1 The success of any sampling program is dependent on proper maintenance of the equipment. Maintenance on the automated sampler and other complimentary equipment is required especially when the equipment is in place for extended periods of time or when sampling multiple events.

6.16.2 Because of the adverse operating conditions associated with sampling (exposure to extreme conditions and events), the equipment should be maintained frequently and after each sampling event.

6.16.3 Perform regular maintenance every time the sampler is set to collect a storm event. Regular maintenance includes, but is not limited to:

6.16.4 Check to make sure all connections are tight.

6.16.5 Inspect the strainer and clear it of debris and sedimentation if necessary.

6.16.6 Make sure tubing is secure.

6.16.7 Inspect sample intake tubing for kinks, cracks, biological buildup, and unusual discoloration and replace if necessary.

6.16.8 If the site to be monitored for extended period, it is recommended to replace the tubing on an annual basis. Other replacement schedules may be required, depending on the specific installation and project requirements.

6.16.9 Inspect pump tubing for wear, cracks, biological buildup, and unusual discoloration. Replace with de-contaminated pump tubing periodically.

6.16.10 Note maintenance activities in field notebook.

6.16.11 Calibrate the auto sampler every time the sampler is set to collect a storm event. Use procedures in accordance with manufacturer specifications.

6.16.12 Rinse tubing with de-ionized water, or site water (i.e., stormwater or ambient water such as base flow).

6.16.13 Check the sampler by collecting a manual sample at the desired setting using the sampler and measure its volume.

6.16.14 Check the sample bottle(s) to verify the desired sample volume was delivered to the sample bottle(s). If not, recalibrate desired sample volume.

6.16.15 Adjust the sample volume to the desired sample aliquot volume according to manufacturer specifications.

6.16.16 Note calibration in field notebook.

6.17 Sampler housing

6.17.1 If the sampler unit is removed or a new unit is placed at the site, the unit should be thoroughly cleaned/decontaminated before placement to prevent cross contamination from previous events or sites.

6.17.2 Inspect desiccant and replace if necessary. This reduces the moisture buildup in the equipment and protects the system electronics.

6.17.3 For sequential sampling, inspect the sample distribution arm and its proper operation.

6.17.4 Check all equipment batteries and replace with freshly charged batteries as necessary.

6.17.5 Note maintenance activities in field notebook.

6.17.6 Decontamination and Cleaning of Equipment (California, 2000 and FL DEP 2004). Specific procedures for decontamination are dependent on analytical parameters to be measured and should be identified in the Project QAPP. The following procedures may need to be modified to conform with a Project QAPP:

6.17.6.1 Before the onset of a new study, thoroughly clean the auto sampler unit(s) using warm soapy water.

6.17.6.2 Rinse the equipment with deionzied water and let air dry.

6.17.6.3 Replace the tubing (if not new) and rinse with deionzed water.

6.17.6.4 Clean the strainer with a brush and soapy water and rinse thoroughly.

6.17.6.5 Clean the pump tube and discharge tube by attaching the suction line and placing the end in soapy water.

6.17.6.6 Manually pump the cleaning solution through the system.

6.17.6.7 Rinse three times with deionzed water and let dry.

6.17.6.8 Clean the suction tubing using the same procedure and rinse with methanol and let dry.

6.17.6.9 Cap ends of tubing with new aluminum foil, tape or laboratory grade cellophane and place in a large sealable plastic bag.

7.0 Records Management

7.1 Keep all field notes and/or field notebook notes on file.

7.2 Be sure to save and back up any electronic notes/files/downloads collected in the field.

7.3 It is recommended to enter the notes into an electronic data system, save and backup the files.

7.4 Keep files available for at least 5 years.

7.5 When using field data forms, create an original and field test the sheet for adaptation to the field procedure. This will help to avoid comprehensive updates. Use a finalized form and update every year.

8.0 Quality Control and Quality Assurance Section

8.1 Blanks (types)

8.1.1 Field rinsate blank.

8.1.2 Equipment rinsate blank.

8.1.3 Bottle blanks.

8.1.4 Trip blanks.

8.1.5 Initial installation blank.

8.2 Duplicates (what type/how many/options)

8.2.1 Separate sampler and flowmeter.

8.2.2 Separate sampler, same flowmeter.

8.2.3 Internal duplicate.

8.2.4 Composite sample split.

9.0 Safety

9.1 There are many hazards associated with sampling stormwater. Some of these hazards include fast moving water, deep water, steep slopes to sampling sites and hostile dogs or people. Use extreme caution when exiting vehicles, walking along busy roads and approaching your sampling site.

9.2 Safety is top priority for field staff and supervisors. A site specific health and safety plan and/or a safety procedure manual will be read and understood by monitoring personnel before site visits are conducted and samples are collected.

9.3 References to help develop safety programs/manuals or site specific safety plans include (see full reference in Section 10.0, Reference Section):

9.3.1 The WSDOT Safety Procedures and Guidance Manual.

9.3.2 WSDOT Work Zone and Traffic Control Guidelines.

9.3.3 WSDOT Pre-Activity Safety Plan (Appendix D).

9.3.4 U.S. Geological Survey, Safety in Field Activities.

9.3.5 Federal Highway Administration's Appendix B, Example Health and Safety Plan.

10.0 References

10.1 City of Tacoma, *Surface Water Management Manual*, September 22, 2008, Volume 3.

10.2 U.S. Environmental Protection Agency, Region 4, *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual*, May 1996.

10.3 Washington State Department of Transportation, *Hydraulic Manual*, Publication M23-03.01, March 2007.

10.4 Washington State Department of Transportation, *Work Zone Traffic Control Guidelines*, Publication M 54-44.01, 2008 http://www.wsdot.wa.gov/publications/manuals/fulltext/M54-44/Workzone.pdf

10.5 Washington State Department of Transportation, "Work Zone Safety Web Site" http://www.wsdot.wa.gov/Safety/WorkZones/resources.htm

10.6 SSFL CDO Expert Panel, *Sample Collection Methods for Runoff Characterization at Santa Susana Field Laboratory*; Robert Gearheart, Ph.D., P.E.; Richard Horner, Ph.D., P.E.; Jonathan Jones, P.E., D.WRE; Michael Josselyn, Ph.D.; Robert Pitt, Ph.D., P.E., BCEE, D.WRE; Michael K. Stenstrom, Ph.D., P.E., BCEE; 10/20/2008.

10.7 U.S. Environmental Protection Agency, Region 5, *Draft TMDLs to Stormwater Permits Handbook*, November 2008.

10.8 *Stormwater NPDES Related Monitoring Needs*, Proceedings of an Engineering Foundation Conference, 1995, Published by the American Society of Civil Engineers.

10.9 Washington State Department of Ecology, *Phase I Municipal Stormwater Permit*, June 17, 2009.

10.10 California Department of Pesticide Regulation, Environmental Hazards Assessment Program, *Standard Operating Procedure: Instructions for Operating ISCO Sampler When Collecting Surface Water*, SOP No. EQWA 005.00.

10.11 Washington Conservation District, Water Monitoring Program, *Standard Operating Procedure (SOP) No. 1: Automated Water Sampling*, Version 2, July 17, 2007.

10.12 U.S. Department of Transportation, Federal Highway Administration, *Guidance Manual for Monitoring Highway Runoff Water Quality*, Publication No. FHWA-EP-01-022, June 2001.

10.13 U.S. Environmental Protection Agency, Office of Water, NPDES Stormwater Sampling Guidance Document, EPA 833-8-92-001, July 1992.

10.14 National Research Council, part of the Water Science and Technology Board, Division on Earth and Life Studies, *Urban Stormwater Management in the United States*, October 15, 2008.

10.15 U.S. Department of Labor, Occupational Safety and Health Administration, 29 CFR Part 1910, standard No. 1910.146(b), accessed August 2009. http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9797

10.16 Water Environment Federation (WEF), *Automatic Stormwater Sampling Made Easy*, Cindy Thrush and Dana B. De Leon, 1993.

10.17 Florida Department of Environmental Protection, *Standard Operating Procedures for Field Activities*, Surface Water Sampling and General Sampling, DEP-SOP-001/01, February 2004 Surface Water Sampling: ftp://ftp.dep.state.fl.us/pub/labs/assessment/sopdoc/2008finalsops/fs2100.doc General Sampling: ftp://ftp.dep.state.fl.us/pub/labs/assessment/sopdoc/2008sops/fs1000.pdf

10.18 California Department of Transportation, Guidance Manual, *Stormwater Quality Monitoring Protocols* (3rd Edition), CTSW-RT-03-109.51.42, July 2000. http://www.dot.ca.gov/hq/env/stormwater/special/newsetup/_pdfs/monitoring/CTSW-RT-03-105/CTSW-RT-03-105.pdf

10.19 U.S. Department of Transportation, Federal Highway Administration, *Guidance Manual for Monitoring Highway Runoff Water Quality*, Publication No. FHWA-EP-01-022, June 2001. http://www.fhwa.dot.gov/environment/h2o_runoff/h2oroff.pdf

10.20 Teledyne ISCO, *6712 Portable Samplers Installation and Operation Guide*, September 15, 2005 http://hampshire.edu/~srNS/Svalbard/Isco%20docments/Isco%206712%20water%20sampler%20users%20manual.pdf

Appendix A Figures 1-3 Types of Composite Samples

Legend
Flow Rate

Rainfall

Demonstration of Aliquot Volume based on 500 ml bottle capacity:

Approximately 100 ml =

Approximately 350 ml =

Approximately 500 ml =

Figure 1: Constant Time/Volume Proportional to Flow Rate or Flow Increment

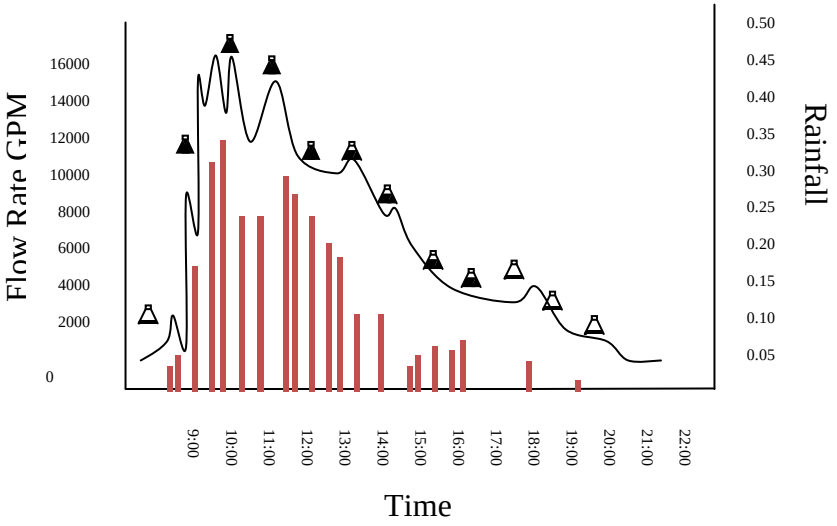


Figure 1 Notes:
Samples are taken at equal increments of time and are composited proportional to the flow rate at the time each samples was taken. Figure 3 Notes:
Samples are taken at equal

Figure 2: Constant Volume/Constant Flow Volume Increment

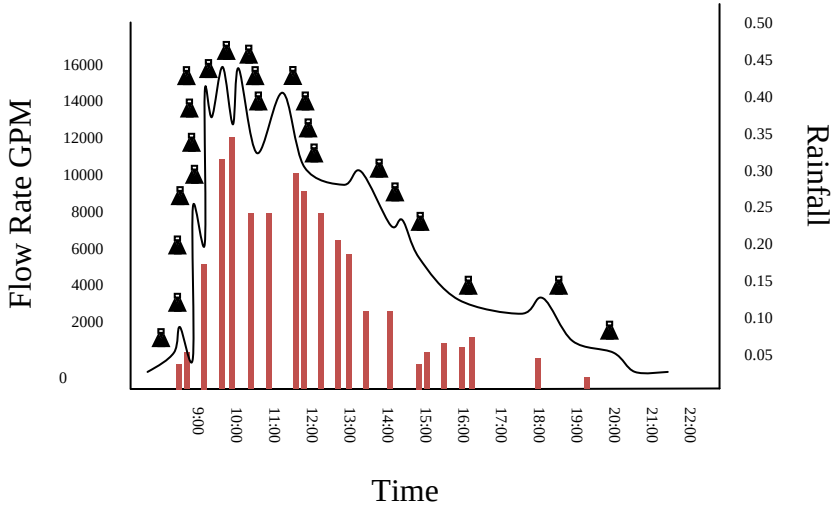


Figure 2 Notes:
Samples of equal volume are taken at equal increments of flow volume and composited.

Figure 3: Constant Time/Constant Volume

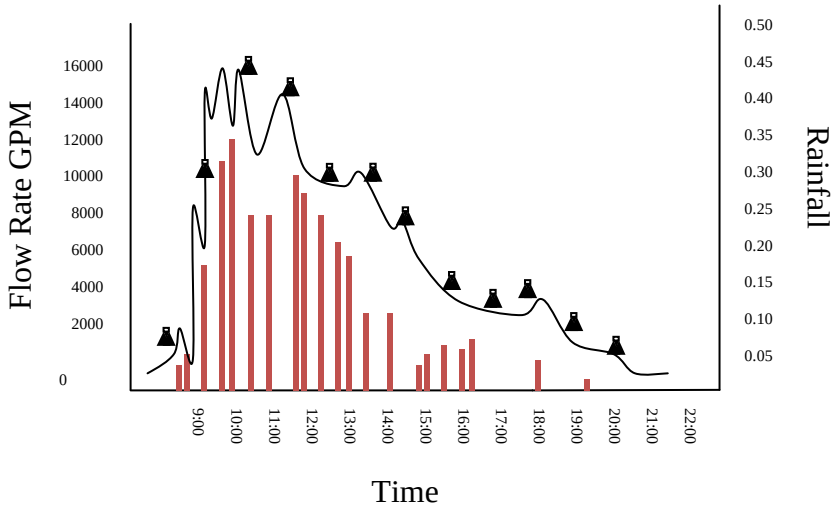


Figure 4 Notes:
Samples of equal volume are taken at equal increments of time and composited to make an average sample.

Appendix B
Estimating Rainfall to Runoff Relationship

Method 1: Estimate your monitoring site/drainage basin characteristics and average storm rainfall characteristics. One advantage of this method is that it provides establishing program elements that will work for a wide range of precipitation amounts. Average storm rainfall is the numeric average such as return frequency of a storm (e.g. Average storm rainfall may be a 5, 10 or 25-year return (i.e. to occur every 5, 10 or 25 years). Rainfall data are available from the National Weather Service.

$$Vr = \frac{PF}{12} \cdot Area \cdot RC$$

Where,
Vr = Runoff volume, cubic feet
PF = precipitation forecast, inches
Area= drainage area, square feet
RC = runoff coefficient

(WEF 1993)

The runoff coefficient (RC) is the overall ratio of runoff to rainfall. It converts rainfall data to an estimated runoff volume. The RC can be calculated based on the impervious area for the entire basin or for each type of land use within a basin.

$$RC = 0.009 \cdot IMP + 0.05$$

IMP – percent impervious

Method 1 Example:

- Drainage Area = 130 acres (5,662,800 sq feet) with 40% commercial, 20% multi-family and 40% single family land uses.
- Percent impervious for each land use is; commercial at 65%, multi-family at 45% and single family at 25%.
- Average storm rainfall = 0.43 inches

RCs
Commercial: RC = 0.009*65% + 0.05 = 0.635
Multi-family: RC = 0.009*45% + 0.05 = 0.455
Single family: RC = 0.009*25% + 0.05 = 0.257

Storm runoff volumes:
Commercial: Vr = 0.43 in (1 ft/12 in)* 5,662,800 sq feet * 0.635*40%/100 = 51,541 cubic feet
Multi-family: Vr = 0.43 in (1 ft/12 in)* 5,662,800 sq feet * 0.455*20%/100 = 18,465 cubic feet
Single family: Vr = 0.43 in (1 ft/12 in)* 5,662,800 sq feet * 0.275*40%/100 = 22,321 cubic feet

Total Runoff Volume = 51,541 cubic feet + 18,465 cubic feet + 22,321 cubic feet = 92,327 cubic feet.

Method 2: This method calculates the flow quantity for one particular precipitation event. Flow quantities can be estimated for a range of precipitation events and each used to calculate a range of program parameters.

$$V_r = \frac{PF}{12} \cdot Area \cdot RC \quad \text{or}$$

$$V_r = \frac{PF}{12} \cdot \left[\left(Area_{pervious} \cdot RC_{pervious} \right) + \left(Area_{impervious} \cdot RC_{impervious} \right) \right]$$

V_r - Runoff volume, cubic feet
PF – precipitation forecast, inches
Area – drainage area, square feet
RC – runoff coefficient, fraction of total precipitation volume delivered to the area that ends up as stormwater runoff at the point of discharge .Single number estimated to represent entire basin or percent pervious and impervious with associated areas of each.

(California DOT, 2000)

Method 2 Example:
Monitoring Site Characteristics:

- Drainage Area = 130 acres (5,662,800 sq feet) with runoff coefficient RC = 0.6
- Average storm rainfall = 0.43 inches

- Storm runoff volume:
- V_r = 0.43 in (1 ft/12 in)* 5,662,800 sq feet * 0.6 = 121,750 cubic feet

Appendix C Estimating Time of Concentration

Example Method 1: The time of concentration is estimated using SBUH methodology (Tacoma 2000). This method is described in the City of Tacoma's *Surface Water Management Manual, September 22, 2008 Edition, Volume 3* (Tacoma 2008). The Time of Concentration, Tc, is defined as:

$$T_c = T_1 + T_2 + ...T_n$$

$$T_t = \frac{L}{60 * V} \quad ; \quad V = k_r \times \sqrt{s_0}$$

Where:

T_c = time of concentration (minutes)
$T_{1,2...n}$ = travel time for consecutive flowpath segments with different categories or flowpath slope (minutes)
T_t = travel time for each segment (minutes)
L = the distance of flow across a given segment (feet)
V = average velocity across the land cover (feet per second)
k = velocity factor (feet per second); see Table 33 with values for sheet, shallow and channel flow)
s = slope of flow path (feet/feet)

Example Method 2: Time of concentration is estimated based on methodology described in the Hydraulic Manual published by the Washington State Department of Transportation (Publication M23-03.01, March 2007) (WSDOT 2007) using the following equations:

$$T_c = T_{t1} + T_{t2} + ...T_{tm}$$

$$T_t = \frac{L^{1.5}}{K\sqrt{\Delta H}}$$

T_c = time of concentration (minutes)
T_t = travel time of flow segment (minutes)
m = number of segments
L = length of segment (feet)
H = elevation change across segment (feet)
K = Ground cover coefficient in feet (meters)
S = slope of segment ($\frac{\Delta H}{L}$) (feet per feet)

Appendix D Pre-Activity Safety Plan

PRE-ACTIVITY SAFETY PLAN

WETLAND ASSESSMENT *(UPDATED12 MAY 09)*

SITE:

Date:_____ Employee:_____

1. Complete pre-travel checklist prior to travel.
2. Plan for drinking water per WAC 296-62-095
3. Review / discusses the Pre-activity Safety Plan controls for each safety hazard identified on the completed hazard assessment checklist with all staff in the field.
4. Team lead maintains completed safety hazard checklist until all have checked in with their supervisor. Save document in the project folder for the next person or time that site may be visited.
5. Fill in the registration sheet (last sheet of this document).

Location: SR_____MP_____ County _____
Region Contact:_____
Phone #: (____) _____ - _____
Nearest Medical Facility: _____
Traffic Control Needed yes no
Cell Phone Service yes no
Closest phone:
_____
_____

Parking Location: SEE PAGE 5

Pre-Travel Checklist

CHECK WITH REGION TRAFFIC MANAGEMENT CENTER ABOUT RUSH HOUR SHOULDER CLOSURES

Traffic Control Plan
Environmental Safety Hazard Assessment and Mitigation Booklet
Washington State Hospital List
Pre-Trip Vehicle Inspection and Familiarization
1st Aid Kit
Flares/Triangles/Signs
Radio Contact List
Emergency Contact Phone List
Beacons/signage/traffic cones available in vehicle
Check SR View for parking possibilities
(http://www.srview.wsdot.wa.gov/home.htm)

PPE's
Vest
Hard Hat
Eye Protection
Gloves
Work Boots
Hearing Protection
Drinking Water
Hip Boots or waders
PFD
Throw rope bag
Sunblock
Insect repellent
Other: _____

Task/Hazard	Control	Site Specific Comments	Requirements
1. Walking over uneven terrain. Yes No	1. Be aware of loose material, excavation drop-offs, tripping hazards (ruts, holes, etc.), uneven ground and other obstructions. 2. Move carefully in areas with the potential for slips, trips, or falls. 3. Wear appropriate footwear with adequate traction and support.		Work boots Leather gloves (Optional put recommended in areas where blackberries are dominant)
2. Working on or around rip-rap Yes No	1. Evaluate rip-rap for loose, rolling, or unstable rocks. 2. Wear hard hat and evaluate need for leather gloves when loose or unstable rock conditions exist or when there is potential for falling rocks.		Work boots and gloves
3. Working in noisy area Yes No	1. Wear hearing protection if sustained noise is at or above 85db (for example next to a freeway, or if you have to shout to be heard by a person 3 feet away from you).		Hearing Protection needed

* The PASP's shouldn't include medical information. If employees elect to volunteer medical information to their supervisor and/or crew that's allowed, but the supervisor and/or crew shouldn't be soliciting that information and it **should not be recorded on this form**. If a worker volunteers information to co-workers or supervisor you can discuss options if that issue arises, but if they choose not to let anybody know it's their prerogative

Task/Hazard	Control	Site Specific Comments	Requirements
4. Bridge Work Yes No	1. Reference controls for: -Walking over uneven terrain -Working around a stream -Working around natural/manmade overhead hazards -Working around fall hazards 2. Coordinate with Maintenance personnel when working from bridge structures. Follow site specific PASP as required. 3. Box girder bridges may have confined spaces requiring training.		Hard hat
5. Working around bridges, signs, light fixtures, power lines Yes No	1. Continuously assess potential for falling rock or other overhead hazards, especially in windy weather. 2. When possible, avoid, restrict time in, or work during times of least activity in hazard areas. 3. When in hazard area, wear hard hat, gloves, and safety glasses along with approved vest and footwear.		Hard hat, gloves, boots
6. Isolated sites / 'bad neighborhoods' Yes No	1. Consider whether location warrants two people or a team to minimize exposure time. 2. Have cell phone or check-in plan in case of emergency.		Two people on site Cell phone
7. Potential for confrontation with adjacent landowner Yes No	1. Evaluate the need for informing local residents of purpose of field work. 2. If an adjacent landowner is known to be problematic, evaluate providing a written or phone notice prior to the visit. 3. If confronted by a disgruntled landowner, speak calmly and leave the site. If threatened, in addition to the above, contact police, as well as your supervisor.		Known problematic land owner: Name: _____ Location: _____ Phone #: _____
8. Potential for transients or human biohazards Yes No	1. Avoid confrontations with transients. 2. Avoid contact with human waste, needles, or other drug paraphernalia. 3. Request assistance from maintenance to remove hazard, when necessary.		
9. Potential for confrontation with a domestic animal Yes No	1. If there is a known potentially dangerous animal on or around the site, contact the person responsible for that animal prior to visit. 2. Consider carrying a deterrent such as a shovel, whistle or mace. 3. If harmed, or confronted with the threat of harm, contact animal control, as well as your supervisor.		Known problematic animal: Owner: _____ Location: _____ Phone #: _____

Task/Hazard	Control	Site Specific Comments	Requirements
10. Poisonous snake or large carnivore hazard Yes No	1. When working in a snake or large carnivore area, consider two or more people for site visits. 2. When in carnivore habitat, make your presence known by talking, whistling, etc. 3. Stay in sight of partner or in radio contact.		Two people on site Radios
11. Harmful / poisonous plants Yes No	1. Be aware of what poison ivy/oak looks like (http://poisonivy.aesir.com/ has many images and information). 2. Be aware of potential for injury from vegetation around you. 3. Bring hand-pruners and glasses to prevent injury in thick brush and briers.		Hand pruners Eye protection
12. Risk of insect / invertebrate problems Yes No	1. Determine if field staff are allergic to bees or yellow jackets. Bring appropriate first aid. Confirm location of nearest hospital. 2. Listen and look for bees frequently in the air and on the surface. When spotted, inform others in the field of the location. Evaluate carefully flagging location for future visits.		Person with allergy?
13. Working around natural overhead hazards. Yes No	1. Assess potential for falling rock or other overhead hazards. 2. When possible, avoid or restrict time in the hazard area. 3. When in hazard area, wear hard hat, gloves, and safety glasses along with approved vest and footwear. 4. Request assistance from maintenance to remove hazard, if possible.		Hard hat, gloves, boots
14. Working around fall hazards* Yes No	1. Do not work in the fall hazard area without appropriate safety equipment and training. 2. Observe fall protection rules in WAC 296-155 Part C-1**. Prepare a fall protection plan, WSDOT form 750-001, prior to performing the work		Fall protection plan needed
17a. Hot weather - Is forecast is for >77 degrees? *** Yes No	1. Consider field partner. 2. Wear weather appropriate clothing. 3. Bring sunscreen and hat for sun protection. 4. Rest as needed; take off hat and vest on breaks. 5. Replenish fluids (drink 1 quart per hour). 6. Stay in sight of partner or in radio contact. 7. Evaluate team for heat-related illness and monitor for need of medical attention	Note in Safety Meeting documentation	Two people on site Radios Hat, sunscreen Drink fluids
17b. Cold weather Yes No	1. In very cold/snow/stormy conditions, consider field partner. 2. Wear appropriate clothing – gloves, hat, thermal underwear, heavy jacket. 3. Stay in sight of partner or in radio contact 4. Is the vehicle equipped with chains/traction tires?		Two people on site Appropriate attire Vehicle equipped with appropriate cold weather gear

** Fall hazard area: An area where you may loose your footing, slide, trip, or loose balance.
* WAC 296-155 is available at: http://apps.leg.wa.gov/WAC/default.aspx?cite=296-155-24501
***Outdoor Heat Exposure WAC: http://www.lni.wa.gov/rules/AO06/40/0640Proposal.pdf

Task/Hazard	Control	Site Specific Comments	Requirements
18. Working in or around areas of shallow or slowly moving water Yes No	1. Evaluate water depth hazard. 2. Evaluate slippery/steep/hidden water edge conditions and need for avoidance or uphill partner. 3. Evaluate large woody debris hazard at the work site and down stream of it. 4. Assess depth of mud and evaluate safe exit. 5. Evaluate potential rescue options that are safe for the rescuer. When warranted, establish person with throw rope bag down slope of work area and between work area and any downstream hazard.		
19. Working <u>around</u> a stream defined as a water hazard (currents greater than 10cfs or deeper than 1-ft) Yes No	1. Evaluate potential rescue options that are safe for the rescuer. 2. Evaluate need for additional support from maintenance, bridge boat, or dive crews. 3. When appropriate, establish person with throw rope bag down slope of work area and any downstream in-channel hazard.		Throw rope bag Hip boots or waders PFD
20. Working <u>in</u> a stream defined as a water hazard Yes No	1. No wading under hazard conditions without safety equipment and training or specialized crews. 2. For in-water work, wear hip waders, tight-fitting neoprene chest wader, or equivalent. In rocky areas, boots with slip resistant felt-like material soles are recommended. 3. Wear personal flotation device in swift/deep water conditions.		

Tool Used	Control	Site Specific Comments	Requirements
1. Shovel	1. Wear gloves, keep handles in good condition or replace.		Gloves
2. Soils knife	1. Point away from bodies, sheath when not in use.		
3. Shears/clippers	1. Keep fingers clear of blades		

PARKING ISSUES **IF WORK OR PARKING IS ON PAVEMENT, SEE LANE CLOSURE REQUIREMENTS IN M54-44. Copy of pertinent parts of M54-44 are in vehicle.** Park in areas that provide safe entrance and exit of the work area, do not create potential conflicts with other vehicles and equipment or fire hazard on tall grass.		
1. SHOULDER CLOSURES: Park and/or work on roadside <15 ft. from edge of pavement more than 1 hour Yes No	1. Coordinate with region Traffic Management Center about rush hours 2. Use beacon lights per WAC 204-38* requirements. **3.** Follow the signage and work provisions in the M54-44** for long duration work zones. **USE Chapter 2 - TCP 5 or 6. Keep appropriate TCP with you.** 4. Modify positions of cones if there is limited visibility or curves in road. 5. Evaluate noise level. If over 85db, use hearing protection.	>1 hour = Stationary work zone. **Use signs and cones with beacon lights: TCP 5 or 6** Vest needed Hearing Protection Hard Hat
2. Park and/or work on <15 ft. from edge of pavement less than 1 hour Yes No	1. Use beacon lights if adequate sight distance per WAC 204-38*. Use signs/cones if reduced visibility 2. Follow the signage and work provisions in the M54-44** for short duration work zones - Chapter 3. 3. If high speed and volume, close shoulder as above. 4. Evaluate noise level. If over 85db, use hearing protection.	< 1 hour Short Duration Work Zone, vehicle beacon lights Vest needed Hearing Protection Hard Hat
3. Traffic an issue, but parking and/or work locations are >15 ft from edge of pavement Yes No	1. Face oncoming traffic while on foot. 2. Be aware of or develop emergency escape routes. 3. Always wear appropriate high visibility apparel; minimum is ANSI class II vest. Avoid working alone. 4. Evaluate noise level. If over 85db, use hearing protection.	Vest needed Hearing Protection Hard Hat
5. Walking from vehicle to work area near high-speed lane Yes No	1. When you can not face oncoming traffic while, try to be aware of what is happening behind you. 2. Be aware of or develop emergency escape routes. 3. Always wear appropriate high visibility apparel; minimum is ANSI class II vest. Avoid working alone. 4. Be especially careful of crossing lanes of traffic and uneven footing that could cause falls into traffic lanes. 5. Evaluate noise level. If over 85db, use hearing protection.	Vest needed Hearing Protection Hard Hat

*WAC 204-38 is available at: http://apps.leg.wa.gov/WAC/default.aspx?cite=204-38

** M54-44 is available at http://www.wsdot.wa.gov/publications/manuals/fulltext/M54-44/Workzone.pdf

HQ: Frank Newboles, State Workzone Safety & Mobility Manager (Policy)
Marty Weed, State Traffic Control Engineer (Technical)
Steve Haapala, State Workzone Training Specialist
Marlin Zimmerman, Traffic Operations Engineer (Training)

Registration Sheet

On-site Checklist

1.Specific concerns: allergies and injuries
2.Cell phones on site
3.Prepared for day (water jug full, clothing…)
4.bio or chemical hazards

Biologist Name and Additional Staff Initials	Date	Notes and Concerns

Appendix C
Chain of custody form

STANDARD OPERATING PROCEDURE

for

CHAIN OF CUSTODY

SOP#: ~~01-01-004-001~~104V1

Date of Implementation: May 1, 2004

Supersedes SOP: 01-01-004-000

Approved by:

Supervisor: _____ Date: _____

QA Officer: _____ Date: _____

Lab Manager: _____ Date: _____

King County Environmental Laboratory
322 W. Ewing Street
Seattle WA 98119-1507

Date approved: July 7, 2004
Revision number: 1
File name: AppendixC_Chain of Custody~~Chain of Custody.doc~~~~COC-Draft.doc~~
SOP #: ~~01-01-004-001~~104v1

1.0 SCOPE AND APPLICATION

The following Standard Operating Procedure (SOP) describes the Chain of Custody procedures and documentation steps used at the King County Environmental Lab. Chain of Custody (COC) is the term used for the unbroken trail of accountability that sample integrity has not been compromised. Chain of Custody begins when the sampler collects the sample and ends when the samples are consumed or disposed. This SOP describes the procedures and documentation beginning when the sampler relinquishes the sample and ending at lab disposal or transfer of the sample to another agency.

The guidelines and practices defined in this SOP will apply to all samples received for testing by the King County Environmental Laboratory including those that may be subcontracted or transferred to other labs or agencies. Samples collected by lab staff and transferred to other agencies before being formally received by the lab need not follow these guidelines. Samples generated within the lab (example: QC samples collected during toxicity studies) do not require COC documentation as long as they are generated and kept within the secure area of the lab until disposal.

2.0 ASSOCIATED STANDARD OPERATING PROCEDURES

The following laboratory SOPs are closely related to this procedure:

SOP #	TITLE
11-02-002	Subcontracting Standard Operating Procedure
01-01-003	Sample Management
01-01-007	Sample Disposal

3.0 DEFINITIONS

The following terms are used throughout this document.

Sample Manager (SM) - The person responsible for performing sample login, initial storage, subcontracting and disposal of samples.

Chain of Custody - An unbroken trail of accountability of possession that ensures the physical security of samples. A sample is under custody if one of the following conditions are met:

- It is in your possession.
- It is in your view, after being in your possession.
- You transferred the sample to authorized personnel.
- It is held in a secure area.

- You secured the sample in an appropriate container with custody seals and made arrangements to transport it to the laboratory.

Secure Area - Indicates a location that protects a sample from tampering. In addition to the analysis and storage areas of the lab, the following are considered secure areas: watercraft used for sampling, locked motor vehicles, sample coolers sealed with packing tape and a chain of custody seal.

4.0 RESPONSIBILITIES

4.1 Sample Collection Personnel: All individuals who collect samples are responsible for the custody of samples until they are transferred to a courier, directly to the lab sample managers or into secure storage at the lab. If samples were collected as a team, only one member of the team needs to relinquish the samples. The sampler relinquishing the samples must initiate the appropriate documentation as described in Section 6.

4.2 Sample Managers: The sample managers and all backup personnel are responsible for accepting the custody of all samples delivered to the lab. The sample manager who signs to accept the custody of samples must insure those samples are stored within the secure area of the lab. Sample managers are also responsible for documenting the disposal of those samples tracked for disposal by LIMS.

4.3 Lab Staff: All lab staff are responsible for following the appropriate sample storage practices as described in Section 5.3. All staff are responsible for maintaining the security of the lab by making sure appropriate doors are locked and that visitors are properly escorted when in the secure area of the lab.

5.0 PROCEDURES

5.1 Building Security and Visitor Access

5.1.1 Building Security: Areas within the building where samples are stored, processed or analyzed have been engineered so that all exterior doors are locked at all times. Access is allowed only to staff or other authorized individuals using a key card system. Each staff member or other authorized individual is issued a key card labeled with a unique identification number. The Operating Engineer maintains the key card system and can deactivate individual cards if lost or stolen.

5.1.2 Visitor Policies: All visitors or anyone not assigned a key card, must enter through the public entrance and sign in at the front desk. A visitors badge is given to all visitors who enter the building. Individuals delivering samples to the sample management area are not required to sign in if accompanied by the SM.

Should you be expecting a visitor, please use the following procedures:

- Notify the front desk when you are expecting a visitor.
- Come to the front desk to meet your visitor(s), rather than requesting that they be sent to your work area.
- Take responsibility for your visitors while they are in the facility. It is understood that visitors may at times be unaccompanied; however, it is the responsibility of lab staff in general and the host employee in particular to be aware of the location and activities of visitors.

5.1.3 Off hours access:
It is expected that only lab staff or authorized personnel with key cards are allowed access to the lab outside of regular business hours.

5.2 Sample Delivery

5.2.1 Regular delivery: The possession of the samples is directly transferred from the sampler or delivery person to the SM or their representative. The appropriate documentation (see Section 6) must be completed by both the sampler and the SM. The date and time of relinquishing and accepting the samples should be identical. The SM is responsible for placing all samples within the secure area of the lab.

5.2.2 After-hours delivery: It is understood that samples will sometimes need to be delivered to the lab after-hours and on those limited occasions when no sample manager is available during regular business hours. Only staff who have access to the secure area of the lab are to deliver samples after hours. For these occasions, the person delivering the samples must place the samples within the secure area of the lab, preferably within the Sample Login Cooler. The person relinquishing custody must sign and date the COC document and leave the original paperwork in the After-hours file holder. Samples should never be left unattended in the Cage area (just inside the exterior entrance to sample login) unless they are contained in sealed coolers (see section 5.2.3). This area is intended as an accessible work place for samplers and not a secure storage location.

5.2.3 Commercial courier deliveries: Delivery of samples using commercial courier services requires that the samples be shipped such that the security of the samples may be verified by the person receiving them. This is accomplished by attaching signed and dated custody seals to the lids of the cooler or other exterior container. The COC documentation must be within one of the sealed

coolers with the samples and is to be signed and dated by the originator just before the container was sealed. Custody seals are available from the lab upon request. It may be necessary to transfer samples to a third person for delivery to the lab. If samples are not within a sealed container, all sample transfers between sampler and delivery personnel must be documented using the Field Sheet or Work Order Form.

5.3 Secure Storage of Samples

Once the samples have been formally accepted by the SM, as defined by signing and dating the appropriate COC form, the samples are considered in the custody of the lab. All samples must be stored in the secure area of the lab, under conditions appropriate to the particular analysis. The storage locations for samples are described in the Sample Management SOP. Extracts or other intermediate products of sample analysis must also remain in the secure areas of the lab. Transfers to and from storage within the lab need not be documented except for those practices used to document sample analysis (benchsheets or instrument logs). Analysts and other authorized staff are allowed unrestricted access to the samples without requiring additional documentation of the transfer of possession.

5.4 Disposal

Disposal and recordkeeping of all samples must follow the guidelines in the Sample Disposal SOP.

5.5 Subcontracting

Samples that are in the possession of the lab and are to be subcontracted or transferred to another lab or agency are to be relinquished by the SM. The SM will complete a Subcontract Chain of Custody form (Section 6.3) for each set of samples released from the lab. Coolers and other containers used to transfer the samples must be secured with custody seals unless the delivery person signs the Subcontract Chain of Custody form before the samples leave the lab. Refer to the Sample Management SOP for additional details on subcontracting samples.

6.0 DOCUMENTATION AND RECORDS STORAGE

6.1 COC Forms

The minimum information for COC documentation is defined as:

- Sample ID (L#s or client ID)
- Signature of person relinquishing samples
- Signature of person accepting the samples
- Date and time relinquished
- Date and time accepted

The exact format of COC documentation can be flexible as long as all the above information is included. For samples that are either collected by King County personnel or are arranged for collection through lab personnel, the following forms are to be used:

6.1.1 Field Sheet

A Field Sheet is a form (generated by LIMS or PIMS) that contains the identification and testing requirements for an individual sample or samples. The bottom part of each page of the field sheet contains blank space for entering all the minimum COC information (as shown in Section 6.1 above). This is typically done with a stamp. Multiple stamps may be added in order to document each transfer of possession before the samples arrive at the lab or if the samples are delivered on different dates or times.

6.1.2 Laboratory Work Order Form

A Laboratory Work Order is a pre-printed form (NCR type) with blank spaces available for writing in the identification and testing requirements for all samples in a submission. The bottom part of each form contains blank lines for entering all the minimum COC information (as shown in Section 6.1 above). A laboratory work order form is typically used when samples arrive without being pre-logged to LIMS or for those samples not to be logged into LIMS.

6.1.3 Subcontract Chain of Custody Form

A Subcontract Chain of Custody Form describes the identification and subcontract testing requirements for all samples shipped from the lab for additional testing or storage. The bottom part of each form contains blank lines for entering all the minimum COC information (as shown in Section 6.1 above). A subcontract chain of custody form must be used whenever samples in the custody of the lab are released for outside analysis. This form may also be used whenever transferring possession of samples outside the lab.

6.2 Records Storage

All documents, including logbooks, must be retained according to King County Environmental Lab policies. See the Sample Management SOP for details.

Appendix D

Attended Hydrolab SOP

STANDARD OPERATING PROCEDURE

for

Attended Hydrolab Multiprobe Operation

SOP #:205v4

Date of Implementation: June 7, 2006

Supersedes SOP #02-01-005-003

Approved by:

Author: _____ Date: _____

Supervisor: _____ Date: _____

QA Officer: _____ Date: _____

King County Environmental Laboratory
322 W. Ewing Street
Seattle WA 98119-1507

Date approved: 11/22/2006
Revision number: 4
File name: AppendixD_Field Measurements using an Attended Hydrolab
SOP #: 205v4

1.0 Scope and Application
This Standard Operating Procedure (SOP) describes the use of Hydrolab multiprobe sondes, including maintenance, calibration, routine use, quality control, data reporting and data review. This SOP applies to attended field operations in both fresh and salt water. These guidelines may not apply to projects where a dedicated Hydrolab is utilized for unattended, long-term data collection.

Parameter	MDL	RDL
Depth	N/A	N/A
Temperature	N/A	N/A
pH	N/A	N/A
Conductivity	.5	10
Chlorophyll a – DS5 Only	.5	1
Dissolved Oxygen – mg/L	.5	1

2.0 Associated Documents and SOPs
- **2.1** Offshore (marine)Water Column Sampling SOP #02-02-002
- **2.2** Lakes Water Column Sampling SOP #02-02-003
- **2.3** River and Stream Water Sampling SOP #02-02-004
- **2.4** ESS LIMS Use and Data Entry SOP #02-03-0070-001

3.0 Method Summary
The *Hydrolab DataSondes (DS5), Minisondes (MS5 and MiniSonde 4a) multiprobes* (referred to collectively as Hydrolabs) are detectors of in-situ temperature, pH, dissolved oxygen, conductivity chlorophyll *a* (DS5 only), depth and salinity in fresh or saltwater environments. Individual probes for the parameters to be monitored are calibrated before field measurements are made. Quality Control (QC) measurements are performed, depending on the parameter, to help determine if acceptable precision and accuracy are being achieved. Sample data can be collected electronically and downloaded to LIMS, or stored in the Data Logger and retrieved later for manual data entry to LIMS. Data are reviewed to insure compliance to QC limits and that downloading was accurately performed. Records are kept on calibration and system maintenance.

4.0 Definitions
pH: pH is the negative log10 of the hydronium ion concentration.

Dissolved Oxygen (DO): The concentration of oxygen dissolved in water, expressed in mg/l or as percent saturation, where saturation is the maximum amount of oxygen that can theoretically be dissolved in water at a given pressure and temperature.

Specific Conductivity: The measure of a water's ability to conduct electricity, and therefore a measure of the water's ionic activity and content, normalized to a temperature of 25 degrees C.

Chlorophyll *a*: Chlorophyll is the molecule in plants that absorbs sunlight and uses its energy to synthesize carbohydrates from CO2 and water.

Chlorophyll *a* sensor: An in-situ optical fluorometer that determines chlorophyll *a* concentrations in a given water sample. The sensor can display the chlorophyll *a* signal as a scaled voltage from 0-5 V or as a concentration from 0-500 μg/L (micrograms/liter). The sensor directly measures the amount of red light emitted by chlorophyll *a* in the water after being irradiated using blue light.

NIST: National Institute of Standards and Technology

5.0 Safety and Hazardous Materials Management

5.1 This method involves the use of corrosive and caustic reagents as well as chemicals that pose contact hazards. Care should be taken to avoid skin contact or inhalation of these chemicals.

5.2 *In-situ* analysis - From a Vessel - Sampling personnel will follow standard safety procedures while on board the sampling vessel. The vessel skipper has ultimate responsibility for safety while the vessel is underway. During deployment of equipment the Hydrolab operator and the skipper (when not the same) must communicate with one another to avoid potential loss of the instrument due to propeller fouling with the underwater field cable.
In-situ analysis – Streams/rivers – Sampling personnel will always enter streams/rivers cautiously and follow standard safety procedures when entering these flowing bodies of water. PFD use is recommended.

5.3 Sample/Reagent Disposal – For disposal of calibration buffers and standards refer to the King County Hazardous Waste SOP # 11-02-003-000. . Reagents or standards that may be used in the field are to be returned to the lab for disposal in the sanitary sewer. The rhodamine WT calibration solution can also be disposed of in the sanitary sewer.

6.0 Sample Containers, Preservation, and Storage

This section is not applicable to this SOP.

7.0 Apparatus, Equipment and Consumables

See section 11 for standards and reagents (consumables).

7.1 Hydrolab Datasonde (DS5)
- **7.1.1** DO probe
- **7.1.2** Conductivity probe
- **7.1.3** Temperature probe
- **7.1.4** pH probe
- **7.1.5** Chlorophyll *a* probe
- **7.1.6** Cyclops-7 Solid Secondary Standard

7.2 Hydrolab Minisonde (MS5 and 4a)
- **7.2.1** DO probe
- **7.2.2** Conductivity probe
- **7.2.3** Temperature probe
- **7.2.4** pH probe

7.3 Hydrolab Surveyor 4 Display Logger (datalogger)

7.4 Sonde to Data Logger field cable

7.5 Digital barometer (Speedtech Instruments)

7.6 Atomic Clock (La Crosse Technology)

8.0 Procedure

8.1 Setup

Connect the sonde and the data logger using an appropriate length cable for the project (5M for streams, longer for lakes). Turn on the logger by pressing the power button in the lower right corner. Ensure that the voltage is at least 7.6 volts. If it is lower, connect it to the charger and use a different logger.

8.2 Calibration

Calibration is typically done in the lab in the following order; dissolved oxygen, conductivity, pH and chlorophyll *a* (DataSonde only). Depth sensor verification is done in the field at the first site of the day. (Manufacturer recommends this order – lowest to highest conductivity reading to minimize erroneous readings due to cross contamination.) Calibration must be done within 24 hours of the start of field analysis. Pre- and post-calibration values should be recorded on the Hydrolab QC sheet along with the lot numbers for all calibration and check standards used. Project information and the names of each instrument used

should also be recorded. When the calibration is complete, fill the calibration cup with tap water until ready to use.

8.2.1 Dissolved Oxygen

Before beginning, check the condition of the DO membrane. It should be free of bubbles, tears and creases. If not, see section 13.0- Preventative Maintenance. Remember after changing the membrane the probe must soak in tap water 24 hours before calibrating. If the membrane is ok, then proceed.
With the Hydrolab oriented so that the sensors are pointed upward, partially fill the open-ended calibration cup with RO/DI water (11.2.1.3 or 11.2.1.2) slightly below the level of the o-ring used to secure the DO membrane. Gently blot any water droplets from the membrane surface with a Kimwipe and loosely cover the open top of the calibration cup with the cap. Allow the DO response to stabilize (about 15 minutes) record the pre-calibration value then calibrate. Press *Setup/Cal, Calibration, Sonde, DO% :Sat*. Enter the barometric pressure in mm Hg (to calculate mm Hg use the digital barometer to get In Hg and multiply that by 25.4). Press *Done*. Following calibration, record the % saturation value on the QC sheet. The post-calibration % saturation value should be within 1% of 100%.

8.2.2 Conductivity

Rinse the sensors several times with RO water with the calibration cup installed. Then rinse the sensors twice more with a small portion of the conductivity standard appropriate for the expected field conditions. Use 6667 µS/cm (11.2.1.2) for salt water environments and 73.9 µS/cm (11.2.1.3) for fresh water environments. Discard these rinsates and fill the calibration cup with fresh conductivity calibration standard. Once the conductivity reading has stabilized, access the Calibrate menu by pressing *Setup/Cal, Calibration, Sonde,* and *spCond : µS/cm*. Enter the appropriate concentration (usually 6667 or 73.9) of the calibration standard and hit the *Done* key to calibrate. Be sure to record the pre- and post-calibration values on the Hydrolab QC sheet. Rinse the calibration cup with conductivity check standard 2 times and fill with the appropriate Check Standard (either 6667 µS/cm or 73.9 µS/cm). The value must be within 10% of the expected value or the sonde must be recalibrated and rechecked with fresh solutions. Record the measured value of the check standard on the QC sheet..

8.2.3 pH

pH requires a two-point calibration – always calibrating to pH 7 first, then pH 4 or pH10 second. Rinse the sensors 2 times with a small portion of the pH 7 buffer (11.1.1.1). Fill the calibration cup to above both electrodes with fresh pH 7 buffer and allow the response to stabilize. Record the pre-calibration value. Access the calibration menu by pressing *Setup/Cal, Calibrate, Sonde,* and *pH :Units*. Enter the appropriate value and press *Done*. Once calibrated, record the value. Dispose of the buffer and rinse the sensors with water. Then rinse the probe 2 times with a small portion of a second buffer (pH 10 (11.1.1.2) or pH 4 (11.1.1.3)) which will best bracket the expected field conditions. Fill the cup with the second buffer and allow the response to stabilize. Record the pre-calibration value then access the calibration menu and enter the appropriate information. Once calibrated, record the pH response of this second calibration buffer, dispose of the buffer and rinse the sensors well with tap water. Rinse the sensors 2 more times with a small portion of the pH Check Standard (11.1.2). Fill the cup with this check standard and allow the response to stabilize. The response must be within +/- 0.2 pH units of the true value (pH 6.86) or the sonde must be recalibrated and rechecked with fresh solutions. Record the measured value of the check standard on the QC sheet.

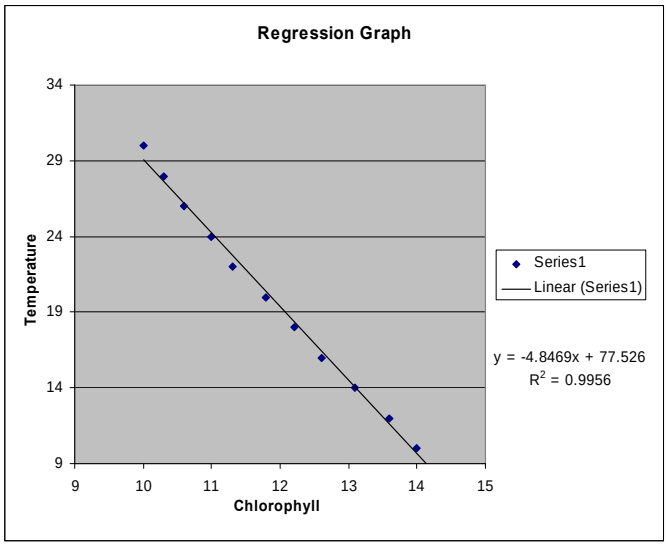
8.2.4 Chlorophyll *a* (DataSondes Only) Calibration Check

The calibration of the chlorophyll *a* sensors on the two DataSondes (DS5) must be checked prior to and after each field run, but daily calibration is not required. For calibration procedures see section 11.3. The calibration check is a two point check. The first point is zero, gathered by submerging the clean sensor in RO water. With the calibration cup in place, thoroughly rinse the sensors off and fill the cup with RO water and securely screw on the cap. Turn the sonde over and rest it on the cap on the bench so that the chlorophyll probe is submerged. Allow the reading to stabilize and write down the value on the QC sheet. For the second point place the sonde in a ring stand and remove the calibration cup from the sonde. Completely dry off the chlorophyll sensor (sides and top) using only a Kimwipe on the lense to prevent scratches. Place the solid standard labeled for the particular sonde onto the sensor, pushing it all the way down and ensuring that ball in the standard engages with the groove on the sensor. It is important to make sure you have the right standard for the sonde – they are not interchangeable. Let the sensor equilibrate for around 30 seconds then record the value in µg/L (micrograms/liter) on the QC

sheet. During calibration the solid standards were set to 5.00 µg/L and should be within 5% for the pre- and post-calibration checks.

8.2.4.1 Chlorophyll *a* Probe Calibration (see section 11.3 for more information)
The chlorophyll sensors require a 2-point calibration which will happen every six to twelve months. These points need to be a zero and a non-zero that is within the range of expected field conditions. The expected chlorophyll *a* values could range from near zero to the mid 20s in micrograms per liter. The fluorescence response of Rhodamine WT changes with temperature. Therefore the temperature of the calibration solution has to be taken, and the chlorophyll equivalent value has to be calculated (based on the table provided by YSI). A linear regression can be created to determine chlorophyll values for in-between-temperatures not shown on the table. Based on the expected chlorophyll *a* range, a Rhodamine value of 0.05 mg/L is used. The table provided by YSI was based on Rhodamine WT concentration of 0.5 mg/L. The equivalent chlorophyll values of 0.05 mg/L Rhodamine WT are shown in the table below.

Temp, °C	µg/L Chl Equiv
30	10.0
28	10.3
26	10.6
24	11.0
22	11.3
20	11.8
18	12.2
16	12.6
14	12.1
12	13.6
10	14.0
8	14.4



Approximate algal chlorophyll equivalent of 0.05 mg/L Rhodamine WT as a function of temperature

To calibrate the fluorometer on the Hydrolab, the zero is calibrated first. Rinse the sonde thoroughly with RO water with the sensor guard attached then submerge in a glass beaker with RO water (plastic can have a fluorescent response so should not be used), allow to equilibrate, then calibrate to zero – press *Setup/Cal, Cal, Sonde, Chlorophyll (µg/L)*, then enter 0 and press done. 0.05 mg/L Rhodamine solution is used for the second point. The temperature of the Rhodamine solution must be taken and the chlorophyll equivalent calculated based on the above table. Temperature can be measured using a NIST certified digital thermometer. This calculated equivalent is what is entered as the second calibration point. Follow the above calibration steps, but enter the chlorophyll equivalent number based on the measured temperature instead of 0.

8.2.5 Temperature
Temperature probe calibration is factory-set and requires no daily calibration. Annually, the calibration must be verified as described in the QC section 9.3.
8.2.6 Salinity
This parameter is a numeric calculation using temperature and conductivity. Therefore, if the temperature and conductivity are within calibration limits, salinity will be properly calibrated. This is not a parameter that is displayed on the Surveyor by default.
8.2.7 Depth

The Hydrolab Sonde has a depth sensor and the user can check the display to raise or lower the probe to the desired depth. If depth is important for the project (lakes for example) the depth sensor calibration must be checked. This is typically done in the field on-site. When holding the Hydrolab above the water, the depth should read 0.0. If it does not, the sensor will need to be calibrated. To calibrate, hold the Hydrolab above the water and press *Setup/Cal, Calibrate,* then *Sonde.* Select *Dep100 :Meters* from the list, enter 0.0 then hit Done. Varify that the reading above the water reads zero, and immersion to one meter yields a correct reading. The sonde should be immersed such that the base of the probe is at one meter. A measuring device such as a marked Secchi disk line can be used to determine the accuracy. Check the appropriate *Depth Calibration* box on the QC sheet..

8.2.8 Internal Clock Calibration Check

Verify that the Data Logger's internal clock is within +/- 30 seconds of the lab atomic clock (see 7.6). The internal clock is reset by pressing *Setup/Cal, Set-up*. Arrow down to *Clock* and press the *Select* button. Verify and/or change the date first *(MMDDYY)* and press *Done.* Change Time *(HHMMSS)* and press *Done* when the atomic clock time agrees with the internal clock time. Check the appropriate box on the QC sheet to document that the time and data have been verified..

8.3 Routine Use - Field Measurements

See KCEL SOPs # 02-02-002, # 02-02-003, and #02-02-004 for measurements made in marine and freshwater systems.

If data will be stored on the data logger a file will need to be created to store the data. Press *Files, Svr4a*, arrow down to *Create* then *Select*, and *Manual* then *select.* Enter the name of the file you wish to create by arrowing with the keypad and selecting the appropriate letters, numbers or symbols. Press *Done* when completed. Choose or verify the appropriate stored parameters by arrowing and selecting (if necessary) *Add* or *Remove*. Press *Done* when completed. Check to see if file has indeed been created by going to file review. If not, re-do and remember to press the *Done* button.

If measurements will be recorded at more than one locator, annotations with locator names should be created prior to storing data at each locator. To create annotations at each locator select *Files,* then *Annotate* then select the file that you want to annotate, then enter the name of the locator by selecting the appropriate numbers and letters then hitting *Done*. Hit *Go Back* to return to the main screen.

Remove the calibration cup and install the weighted sensor guard. When deploying the Hydrolab in waters flowing at less than one foot per second or 0.25 meters per second, such as a lake, activate the stirrer. This provides adequate flow for reliable DO readings. The stirrer is activated by pressing *Setup/Cal, Setup, Sonde*. Arrow down to *Circltr* and press the *Select* button. Arrow to 1, press *Select* then *Done* and the circulator will start. Remember the circulator should be turned off after you are done sampling, during QC work and during streams sampling.

Once the annotation is entered, the probe is adjusted to the correct depth using the depth sensor (Major Lakes project) or in the appropriate location within the stream. Allow the probe to equilibrate (stabilize). Equilibration occurs when the instrument has stabilized enough so that the readings no longer change in a linear direction over the course of a short period of time, such as 20-30 seconds. Although equilibration is subjective, experienced operators can quickly and efficiently recognize equilibration. The *store* key is then pressed to record the data. The locator annotation must be entered before data is stored for each unique location (Multiple depths under one locator annotation are allowed). A macro is available for downloading the electronic Hydrolab data directly in to LIMS, so a unique LIMS number corresponds to the depth automatically, without making annotations in the field. For field duplicates, annotate the locator name including the letters DUP.

The following sequence is to be followed for annotating and storing a typical data point; *Annotate* (write locator code), *Enter* (stores annotation) then *Store* (to store meter readings). Press *Files, Surveyor 4, Annotate (Select),* choose the correct file, then *Select*. Enter the appropriate locator or sample number using the arrow keys and *Select*. Press *Done* when completed. Press *Go Back* twice. When the instrument has equilibrated, press *Store*. Select the appropriate file to store the data to and press *Select*. For some projects,

the readings are recorded on the laboratory fieldsheets. If this is to be done, the analyst should use (retrieve) the data that is logged to the hydrolab rather than writing down real-time data. This will eliminate any discrepancies between the fieldsheet data and the hydrolab electronic data.
Note that the stored Major Lakes hydrolab data will be downloaded electronically into LIMS. Streams data are recorded directly on to fieldsheets, then manually entered in to LIMS.

The probe must be capped during the time between the last field measurement and arrival at the lab and must be stored with sufficient ambient water in the cap to maintain high humidity but not cover the individual probes.

9.0 QA/QC Requirements

9.1 Post-Deployment Calibration QC (End Check)

Calibration QC requirements for typical operation involve determination of post-deployment calibration drift for the parameters of interest. Calibration drift is determined by measuring the check standard solution at the conclusion of the field measurements. This check must be done within 12 hours of the last field measurement. The post-deployment checks must be done in the same order used for initial calibration and must be done before any maintenance or calibrations are performed.

9.1.1 DO Post-Deployment Calibration Check
Set up the sonde as described in 8.2.1. Measure the % DO in the saturated air and record the value.
9.1.2 Conductivity Post-Deployment Calibration Check
Immediately after the DO check, rinse the calibration cup with conductivity calibration check standard then fill the calibration cup with the Conductivity calibration check standard (11.2.2.2 or 11.2.2.3) and record the measured value.
9.1.3 pH Post-Deployment Calibration Check
Immediately after the Conductivity check, rinse the calibration cup with pH calibration check standard then fill the calibration cup with the pH calibration check standard (11.1.2) and record the measured value.
9.1.4 Chlorophyll *a* Post-Deployment Calibration Check
Immediately after the pH check rinse out the calibration cup and all the sensors with RO water. Follow the procedures as described in 8.2.4. to check the zero and non-zero chlorophyll equivalents.

If any parameter falls outside the acceptance limits shown below, the field data collected with the sonde may be qualified. See QA Manual.

Parameter	Calibration End Check
Dissolved Oxygen	± 4 %
Temperature	See below
Conductivity	± 10 %
pH	± 0.2 pH units
Chlorophyll *a*	± 10%

9.2 Field QC

QC for field measurements is typically limited to measuring precision by collection of replicate (FREP) and duplicate (FDUP) field measurements. Replicates are done at a minimum frequency of 5% of measurements or once per day. A field replicate is defined as a separate in-situ measurement made following all procedures typically done between individual samples. The probe would typically be removed from the water body then returned to the same depth and position used in the original measurement. Field measurement duplicates are defined as two sequential measurements made on a portion of the sample collected in a bucket or other container (Turn circulator on or swirl probe slowly.) Again, remove the probe from the bucket/water between readings. If the measurement is not typically

done in a bucket or similar container, the field duplicate values are to be used only for QC purposes. Field duplicates will typically be performed immediately following the field replicates.

To meet project requirements, checks using calibration check standards may also be performed in the field. A pH calibration check standard (11.1.2) and a conductivity calibration check standard (11.2.2.2 or 11.2.2.3) may be taken into the field for each sampling run (Chlorophyll will not be checked in the field). The calibration checks should be analyzed at the same frequency as the field replicates and duplicates (a minimum frequency of 5% of measurements or once per day)

The following table describes the acceptance limits for field duplicates and calibration check standards. Since field replicates may be affected by changing field conditions rather than instrument problems, no acceptance limits have been defined.

Parameter	Duplicate Samples	Field Calibration Check Standards
Dissolved Oxygen	RPD ≤ 20%	Not applicable
Temperature	± 0.3 ^{o}C	Not applicable
Conductivity	RPD ≤ 10%	± 10 %
pH	± 0.2 pH units	± 0.2 pH units
Chlorophyll a	Not applicable	Not applicable

RPD = Relative Percent Difference = $\mathbf{100 \times [(r_1 - r_2)] / ((r_1 + r_2)/2)}$
where r_1 = result 1 r_2 = result 2

9.3 Temperature Calibration Checks

Temperature probe calibration is confirmed at least annually with a side-by side comparison of the probe response at two separate temperatures to a NIST-traceable thermometer. The probes and NIST-traceable thermometer are placed in a container of water that was allowed to equilibrate for 24 hours at room temperature. Once the probe response has stabilized (no longer than 10 minutes), the probe and thermometer readings are recorded in the calibration logbook. The probes and NIST-traceable thermometer are then placed in a beaker of RO water that has been stored overnight in the walk-in cooler at 4 ^{o}C. Once the probe response has stabilized (but no longer than 10 minutes), the probe and thermometer readings are recorded in the calibration logbook. For both temperature points, the probe response must be within ± 0.2 ^{o}C of the measured response of the NIST-traceable thermometer. If not, the meter should be returned to the manufacturer for recalibration.

9.4 Corrective Action

If calibration verification or precision of duplicate field measurements do not meet specifications, these QC measurements should be immediately repeated. Calibration failures that are detected in the field may be corrected by re-calibrating then repeating the calibration verification. If this second verification or duplicate fails, the instrument should not be used for field measurements until the problem is fixed and acceptable performance has been verified. If QC failures are observed, lab analysis may also be used in place of field measurements. It may be necessary to flag the data or repeat the measurements with a properly functioning meter if other corrective actions cannot be performed.
Changing field conditions rather than a malfunction of the field meter may affect replicate field measurements. No corrective actions will be based on field replicates when acceptable field duplicates are observed. Significant changes in barometric pressure may affect the post-calibration values. This change should be documented.
DAF forms should be used when there is any failure of the QC requirements that could have an effect on the data produced by the Hydrolab, when there are unusual field conditions that may affect the expected data, or if any described procedures were not able to be followed for whatever reason.

10.0 Data Reduction, Reporting, Review and Documentation

10.1 Sample Data Entry to LIMS

Any field measurement that is associated with a unique sample number (L#) should be loaded to LIMS. Data entry to LIMS can either be done electronically from the data logger or by manual entry of the numeric values. Data is electronically downloaded from the datalogger and transferred to LIMS for the Major Lakes Project. Manual data entry to LIMS is done using the values entered on the field sheet (Streams Project). Following entry, LIMS data is printed and archived with a copy of the data file from the meter or the field sheet(s) and the hydrolab calibration/QC form.

10.1.1 Electronic Download

Attach a 9-pin serial cable to the Hydrolab Datalogger and to the serial (COM 1) port on a Windows-based PC. Go to Start, Programs, Accessories, HyperTerminal and click on HyperTerminal.
Use COM 1, with the following Port Settings:
BPS = 19200, DB = 8, Parity = None, Stop bits = 1, Flow control = Xon / Xoff.
Under settings, use Auto-detect Emulation, Backscroll buffer line = 500.
With the datalogger on, select "files". On the next menu, select "transmit". In HyperTerminal, select transfer and receive file. Enter the path to store the data file, enter the file name, but don't press "OK". Return to the datalogger and press any key, this will start the file transmit. Click on "OK" in HyperTerminal and the upload should begin.

10.1.2 Manual Data Entry

Hydrolab data can be manually entered into LIMS. During sampling, either log the data (8.3) or write the values displayed from the DataLogger screen onto your project fieldsheet. See SOP # 02-03-007.

10.1.3 DAF Forms

DAF forms should be filled out in hardcopy then filed electronically in LIMS (no procedures currently exist to document the LIMS process). Electronic copies of the DAF form can be saved in K:\ess\qa\DAF Forms with the following format: DAF_ESS_WG*****

10.2 Documentation of QC results

Field QC results and pre- and post-calibration results are to be documented on a Hydrolab calibration sheet, and then photocopied. The original is filed in the Hydrolab QC notebook; a photocopy is turned in to Login with the fieldsheets and added to the data package (10.3). Calibration verification, continuing calibration and post deployment check standards for pH and conductivity are added to LIMS as check standard (CS) samples and verified for compliance within acceptance limits. Duplicate samples are added to LIMS as FDUP samples and calculated for relative percent difference between samples. Replicate samples are samples with unique Login numbers that are also added to LIMS QC as FREP samples and calculated for relative percent difference referencing the original sample number. See SOP # 02-03-007 section 8.2.4 for details on creating QC samples in LIMS.

For standards, the lot number must be recorded with the calibration results. The name of the Hydrolab Sonde and Surveyor that was used for the analysis must be recorded on the QC sheet.

10.3 Data Review

A copy of the LIMS data review report, workgroup report, QC report, field sheet, any DAFs and hydrolab QC form are reviewed by a second individual familiar with the procedure before the data is approved in LIMS. A Review Sheet is completed for each workgroup to document the review process. Hardcopy data is stored with project records for a minimum of 10 years following the collection date.

10.4 Reagent and Standards Preparation Logbook

Conductivity standards preparation is tracked in the conductivity standards binder in the calibration room. All new standards that are prepared must be documented in this notebook.
Chlorophyll *a* equivalent Rhodamine WT calibration standard preparation should also be tracked and documented in the appropriate binder in the calibration room.

11.0 Standards and Reagents

11.1 pH

The following solutions are for single use only and should never be poured back into their original containers. The standards are stable at room temperature. Working aliquots are to be taken from the stock solution and used to calibrate and verify the calibration of the pH sensor. The buffer expiration dates are specified by the manufacturer, while the continuing calibration standard has a shelf-life of 6 months. Please shake all reagents/standards before dispensing.

11.1.1 Calibration Standards

11.1.1.1 pH 7.0 Buffer Standard

Fisher catalogue (#SB107-4 or SB107-20) commercially prepared buffer solution.

11.1.1.2 pH 4.0 Buffer Standard

Fisher catalogue (#SB101-4 or SB101-20) commercially prepared buffer solution.

11.1.1.3 pH 10.0 Buffer Standard

Fisher catalogue (#SB115-4 or SB115-20) commercially prepared buffer solution.

11.1.1.4 Continuing Calibration Check Standard (pH 6.86)

Lab Chem Catalogue (LC12350-5) commercially prepared buffer solution or Beckman catalogue (#BK3006) for in house check standard (CS) preparation. Prepare the check standard according to manufacturer's instructions using the Laboratory's RO water. All pertinent reagent preparation information must be entered into the reagent preparation log, including preparation and expiration dates, volume prepared, etc. Transfer the pH check standard solution to a 1 Liter wide mouthed HDPE bottle. Place a label on the outside of the bottle with the chemical's name and concentration, the analyst's initials, the date of preparation, the expiration date (six months after preparation), and the preparation number. This reagent is stored at room temperature.

11.2 Conductivity

11.2.1 Calibration Standards

11.2.1.1 Dried Potassium Chloride (KCl; Fisher Scientific #P217-3) – Place several grams of KCl on a watch glass and dry it in the oven (103-105 degrees C) for several hours. Place the dried KCl in a dessicator and cool to room temperature.

11.2.1.2 6667 umhos/cm Calibration Standard

Potassium Chloride (KCl) Calibration Standard Stock, 6667 µmhos/cm - In a 1000mL volumetric flask with approximately 800mL RO water, dissolve 3.728 g dried KCl (11.2.1.1); dilute to 1000mL with RO water. In the Reagent Preparation Logbook write the preparation ID #, date, analyst's initials, lot number of the chemical used, concentration of the chemical made, and the date of expiration. This 0.05 M KCl solution has a conductance of 6667 µmhos/cm at 25°C. The solution is stable for one year and is stored in a 5 Liter storage container at room temperature.

11.2.1.3 73.9 umhos/cm Calibration Standard

Working Calibration standard, 73.9 µmhos/cm- Dilute 10mL of the stock KCl solution (11.2.1.2) to 1000 mL in a volumetric flask with RO water. This solution is stable for six months, and is stored at room temperature. In the Reagent Preparation Logbook, record the concentration of the solution, the date, how the reagent was made, and the date of expiration.

11.2.2 Continuing Calibration Check Standard

11.2.2.1 Dried Potassium Chloride (KCl; Fisher Scientific #P217-3) – Place several grams of KCl on a watch glass and dry it in the oven (103-105 degrees C) for several hours. Place the dried KCl in a dessicator and cool to room temperature.

11.2.2.2 6667 umhos/cm Check Standard

Potassium Chloride (KCl) Check Standard Stock, 6667 µmhos/cm - In a 1000mL volumetric flask with approximately 800mL RO water, dissolve 3.728 g dried KCl (11.2.2.1); dilute to 1000mL with RO water. In the Reagent Preparation Logbook write the preparation ID #, date, analyst's initials, lot number of the chemical used, concentration of the chemical made, and the date of expiration. This 0.05 M KCl solution has a conductance of 6667 µmhos/cm at 25°C. The solution is stable for one year and is stored in a 5 Liter storage container at room temperature.

11.2.2.3 73.9 umhos/cm Check Standard

Working Check Standard, 73.9 µmhos/cm- Dilute 10mL of the stock KCl solution (11.2.2.2) to 1000 mL in a volumetric flask with RO water. This solution is stable for six months, and is stored at room temperature. In the Reagent Preparation Logbook, record the concentration of the solution, the date, how the reagent was made, and the date of expiration.

11.3 Chlorophyll *a* Sensor Calibration and Solid Standard Setup

See *Hydrolab Chlorophyll Probe Calibration Report* for more details
The Chlorophyll a sensor calibration will occur at a minimum of once a year, or as often as is needed based on observed drift. This process of calibrating the chlorophyll probes is conducted using Rhodamine WT because the heterogeneous nature of algae-containing ambient water does not produce a stable enough reading to determining a specific voltage response for a given sample. The homogeneity of Rhodamine solution produces a very stable response that can then be correlated with an approximate chlorophyll equivalent. The Rhodamine WT to chlorophyll equivalent was based on tables provided by YSI and is temperature dependent (fluorescence intensity shows an inverse relationship with temperature).

The chlorophyll probe requires a two point calibration using a zero point and a positive standard. RO water (representing zero chlorophyll) and 0.05 mg/L Rhodamine WT are used to calibrate the sensors.

11.3.1 Rhodamine WT Standard

A concentrated Rhodamine WT solution of 106.7 mg/L is made plus 2 dilutions to get to 0.05 mg/L used to calibrate the sensor. The initial concentration of 106.7 mg/L is made based on the specific stock of Rhodamine WT that we have on hand (received 2006): 21.34% by weight (0.5 g/1000 x 21.34% x 1,000,000 = 106.7 mg/L)

From this 106.7 mg/L concentration a 0.5 mg/L concentration was prepared and used to make the functional calibration solution. Below is a table which describes how each was made.

Concentration	**Method**
106.7 mg/L	0.500 grams 21.34% Rhodamine WT brought up to 1000 ml
0.5 mg/L	4.69 ml of 106.7 mg/l brought up to 1000 ml
0.05 mg/L	100 ml of 0.5 mg/L brought up to 1000 ml

Keyacid Rhodamine WT Liquid
21.34% Weight (May 2006 Batch)
Product Code 703-010-27
Keystone Aniline Corp
2501 W Fulton St
Chicago, IL 60612
800-522-4DYE - Jim Brink

11.3.2 Solid Standard Setup

Each sonde has a dedicated adjustable solid standard (Cyclops-7 Solid Secondary Standard) that can be used to conduct continuing calibration checks. This step must take place immediately following the sensor calibration and should not be done at any other time. Calibration is done, at a minimum, once a year.
Once the sensors had been calibrated the standards can be set to whatever chlorophyll value is average for expected field conditions (currently set to 5.00. µg/L). Because each sensor has a slightly different voltage response for similar chlorophyll values, there is a dedicated standard for each sensor – they are not interchangeable. To set up the solid standard, attach the correct standard to the chlorophyll sensor on the same name Sonde – ensure that the sensor is clean and dry and that the standard is aligned properly with ball resting in the groove. Insert a standard flat head screw driver into the top of the solid standard and unscrew the locking nut as far as it will go. Next, to change the signal response, use a small green screw driver provided and insert the blade through the hole in the locking nut. Rotate it until it engages with the adjustment screw that is beneath the locking nut. Adjust the screw until the signal response reads as close to 5.00 µg/L as you can get it. Now use the larger flat head screw driver to lock the locking nut down. As you tighten the locking nut, the signal response may change. You may need to adjust the standard so that when the locking nut is tight the response is 5.00 µg/L. Calibration is documented in the applicable notebook in the calibration room.

11.4 RO Water

RO Water – reverse osmosis water; ASTM Type I

12.0 Contamination

Aside from algal growth, there are a number of factors that may cause inaccurate sensor readings such as inadequate equilibration time, improper calibration, and instrument damage due to travel. Calibration drift can occur on all sensors.

13.0 Preventative Maintenance

To ensure continued and reliable Hydrolab operation, thorough and regular maintenance of the probes must be performed. Make regular visual inspections of the equipment and sensors, compare pre- and post- calibration results and monitor the sensors' response time. Record results on appropriate QC forms. See users manual for more detailed preventative maintenance instructions.

Storage caps and rubber dummy plugs appropriate for each sensor must be in place during storage and transport to and from the field. Add a small amount of tap water to the storage cup to keep the sensors moist during times of storage and transport.

When DO calibration becomes impossible (fails) or when the membrane covering the cell becomes wrinkled, bubbled, torn, dirty or otherwise damaged then DO sensor maintenance is required. See users manual. Allow membrane to soak overnight in tap water before calibration. The electrodes should be checked for corrosion and lightly sanded according to manufacturers specifications (see Hydrolab Operating Manual). Use a cotton swab with soap and water to clean the glass of the pH probe and the holes inside the conductivity probe.

Slow or drifting responses during calibration or field measurements would indicate electrode maintenance or replacement might be necessary. See the instrument manual for troubleshooting and maintenance procedures.

The chlorophyll sensor top can be wiped clean prior to deployment but only using Kimwipes to that the sensor does not get scratched.

Maintenance must be recorded in the Maintenance and Repair Log book in the appropriate section for each probe.

14.0 Training Outline

New analysts must successfully perform initial calibration, QC checks, data logging, and end check data review under the direct supervision of an experienced analyst.

15.0 References

Hydrolab Operating Manual
Turner Designs "Using the Cyclops-7 Solid Secondary Standard
Hydrolab Chlorophyll *a* Sensor Instruction Sheet

Appendix E

KCEL Sealogger CTD SOP

STANDARD OPERATING PROCEDURE

for

SBE 25 SEALOGGER CTD

SOP # 220v3

Date of Implementation: February 28, 2005

Supersedes SOP: 02-02-011-002

Approved by:

Author: _____ Date: _____

Supervisor: _____ Date: _____

QA Officer: _____ Date: _____

King County Environmental Laboratory
322 W. Ewing Street
Seattle WA 98119-1507

Date approved: 11/22/2006
Revision number: 3
File name: AppendixE_Sampling and Field Measurements using SBE 25 Sealogger CTD
SOP #: 220v3

1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the use of the Seabird SBE 25 CTD and LI-COR LI-1400 DataLogger, including maintenance, calibration, routine use, sample collection, quality control, instrument programming, data upload, reporting and review. This SOP applies to attended field operations. Two CTD configurations are possible; one using the CTD independently and the second incorporating the AFM (Auto-Fire Module) to simultaneously collect water quality samples. The CTD instrument and calibration is optimized for marine work but can be utilized in fresh water for physical water sample collection. Fresh water analysis using CTD sensors is not recommended for two reasons: (1) the conductivity probe is calibrated for high salinity water bodies and does not have the dynamic range to accurately measure fresh water conductivity levels and (2) the instrument is designed to move quickly through the water column which is not conducive for accurately measuring extreme thermoclines that often occur in fresh water bodies such as Lake Washington.

2.0 ASSOCIATED DOCUMENTS AND SOPS

2.1 KCEL Sampling Methods for Marine Water Column: 02-02-002-003
2.2 KCEL Sampling Methods for Water Column of Lakes: 02-02-003-001
2.3 KCEL C-14 Study Nutrient and Chlorophyll Sampling: 02-02-010-001
2.4 KCEL CTD File Handling Protocol (see appendix at the end of this SOP)
2.5 KCEL Oxygen, Dissolved -- Winkler Titration, Azide Modification : 03-03-007-002

3.0 METHOD SUMMARY

The *SBE 25 SEALOGGER CTD* (referred to as CTD) is a profiling system for lake, coastal, estuarine, and deep water work. In addition to monitoring conductivity, temperature, pressure, derived salinity, density, dissolved oxygen, chlorophyll, light intensity (PAR)and light transmission, the CTD also utilizes a carousel (rosette) of sample bottles capable of collecting up to 12-five liter samples. Additional sensors can be added to analyze more or different parameters. Individual probes for the parameters to be monitored are calibrated annually at the factory or, in the case of dissolved oxygen and light transmission, monthly based on laboratory Winkler dissolved oxygen results and transmissometer calibration. The LI-1400 DataLogger is a simple data collection instrument with a remote radiation sensor attached. For both instruments, data is collected electronically and uploaded to a PC. Sample data are downloaded to LIMS. Daily logbooks are kept, along with calibration and system maintenance records.

4.0 DEFINITIONS

4.1 Conductivity, Temperature, Depth Profiler (CTD): An instrument capable of profiling conductivity, temperature, and depth (pressure) throughout a water column.
4.2 Auto-Fire Module (AFM): The AFM allows Carousel operation without a conducting sea-cable by firing bottles at user programmed time intervals, or when used with SBE 25 CTDs, the AFM monitors CTD pressure data and fires bottles at user-programmed depths. The AFM also records bottle number, firing confirmation, and 5 scans of CTD data for each bottle fired.
4.3 Fluorometer: Optical instrument used for the detection of chlorophyll and other pigments that fluoresce in the selected wavelength range.
4.4 Light Intensity (see PAR): Measurement of solar energy in units of $\mu mol\ s^{-1}\ m^{-2}$.
4.5 PAR: Photosynthetically Active Radiation
4.6 Dissolved Oxygen (DO): The concentration of oxygen dissolved in water, expressed in mg/l or as percent saturation, where saturation is the maximum amount of oxygen that can theoretically be dissolved in water at a given altitude and temperature.
4.7 Temperature/Conductivity (TC) Duct: Plastic duct though which an exact amount of water is pumped at a constant rate in order to produce a consistent time delay between the temperature and conductivity sensors. This time delay can then be corrected when calculating water column parameters.
4.8 Bottle Data: The .afm file stores the exact time each bottle is tripped. Using the Seabird Data Processing Software, CTD data can be related and compared directly to the physical water collected.

4.9 RO Water: Reverse osmosis water (de-ionized water).
4.10 Nickel-Cadmium (Nicad) Battery: 12 volts at maximum charge; CTD shuts down at 7.4 volts. Alkaline Battery: 13.5 volts fresh.
4.11 Transmissometer: An instrument used in the measurement of light transmission though water in units of % transmission.
4.12 Density is calculated from in situ measurements of pressure, temperature, and conductivity using the equation of state for sea water. The units are defined as kg/m^3. (description and units)
4.13 Chlorophyll: The WETStar miniature fluorometer allows the user to measure relative chlorophyll by directly measuring the amount of fluorescence emission from a given sample of water. Specifically, it measures the fluorescence of chlorophyll-containing phytoplankton, which absorb light of wavelengths between 400 and 520 nm and emit light between 670 and 730 nm. The instrument is calibrated at the factory on an annual basis.

5.0 SAFETY AND HAZARDOUS MATERIALS MANAGEMENT

All sampling personnel will follow standard safety procedures while on board the sampling vessel. The vessel skipper has ultimate responsibility for safety while the vessel is underway. During deployment and retrieval of the CTD, the boom operator takes responsibility for safety on the back deck of the vessel. Sampling personnel are required to wear steel-toed footwear during deployment and retrieval of the CTD.

No hazardous materials are associated with this method of sample collection and *in-situ* analysis except for **Alkali-Iodide-Azide (AIA)-** AIA is a poisonous and caustic liquid reagent used for Winkler dissolved oxygen fixation. Contact with skin must be avoided. AIA must be stored in a well ventilated, dry, and cool area. Working reagents will be stored in a re-pipet dispenser. Always wear gloves and safety glasses when working with AIA.

6.0 SAMPLE CONTAINERS, PRESERVATION AND STORAGE

See appropriate method SOPs if water quality samples are to be collected and analyzed.

7.0 APPARATUS, EQUIPMENT, AND CONSUMABLES

7.1 Seabird SBE 25 Sealogger CTD
7.2 Seabird SBE 32 Carousel Water Sampler
7.3 Seabird Auto-Fire Module
7.4 Seabird SBE 29 Pressure Sensor
7.5 Seabird SBE 3 Temperature Sensor
7.6 Seabird SBE 4 Conductivity Sensor
7.7 Seabird SBE 5T Pump
7.8 Seabird SBE 43 Dissolved Oxygen Sensor
7.9 WETlabs WETStar Chlorophyll Fluorometer
7.10 WETlabs Seastar Transmissometer
7.11 LI-COR Light Intensity (PAR), LI-193-SA
7.12 LI-COR Surface Light Intensity (PAR), LI-190-SA-50
7.13 LI-COR LI-1400 Data Logger
7.14 Laptop computer with Microsoft Windows
7.15 Seabird SeaTermAF, Seasave-Win32, and SBE Data Processing-Win32 software
7.16 Replacement Ni-Cad Battery (PN 80256)
7.17 Deck crane with meter wheel
7.18 100 ml syringe with tube

8.0 PROCEDURE

8.1 CTD with AFM and Rosette

8.1.1 Prior to the first cast of the Day

Disconnect the dummy plug on the AFM bulkhead connector and insert the 10 meter four pin data I/O cable (801616). Connect the opposite end of the I/O cable to the 9 pin serial port on the PC. In Windows, open SeaTermAF Click on the Connect CTD Button. An S> prompt should appear. Note the connection is using a baud rate of 4800.Type st and press Enter. This will prompt you for the correct time. Type in the time using the following format; e.g. 134325 is 1:34:25 pm. Press Enter and type the date; e.g. 091006 is September 10, 2006. Press Enter. Click on the Status button. The important things to look for are the vmain (the nicad battery stops working below 7.4 volts), the vlith (this should be >5 and can be replaced only by the factory), the minimum frequency for pump turn on (3500 for salt water, 2000 for fresh water), and the correct time and date. If the main battery voltage is low, replace with either a freshly charged nicad battery or new alkaline batteries (use cc if changing battery types). If the minimum frequency for pump turn on is incorrect, use the cc command to adjust to the correct setting. The date and time should be calibrated between the AFM, CTD, and Li-Cor based on the atomic clock in the calibration room. Each of the instruments should be within one second. Switch to the AFM by clicking on the Connect AFM button. Type st as above to correct the AFM time.

8.1.2 Programming CTD

In Sea-TermAF, click on the Connect CTD button. If the minimum frequency to turn pump on is incorrect, adjust it according to 8.1.1. At the S> prompt, type il to initialize logging. Click on the Init Log button. This changes the ncast to 0 and prepares the instrument for the upcoming cast. Wait for about 5 seconds until a message box confirms the CTD is ready to go. . .

8.1.3 Programming AFM

Click on Connect AFM and the A> prompt should appear. Click on the Configure Menu and then AFM with SBE 25. Make sure the current CTD instrument configuration (.con) file is being used. Monthly, a new configuration file is created following calibration. Real time baud rate is always 4800 and radio button is either on **Close on upcast** or **Close on elapsed time, record CTD Data**. Use the latter setting only for very shallow stations that require multiple bottles tripped at the same depth.

8.1.3.1 Close on Upcast

8.1.3.1.1 Option one is to close the first bottle at the bottom of the cast after it has been sitting stationary for one minute. Check the **Bottom bottle closure enabled** box, set **Pressure to Enable Upcast** to 0.5xdepth. Pressure Change to Enable upcast is 2, Stationary time on Bottom is 1 minute and Bottom Pressure Window is 3. Click on the Bottle Closure Pressures/Times tab and select the Number of Bottles to Close and type the closure pressures.

8.1.3.1.2 Option two is to close the bottom bottle with no wait at the end of the downcast. Uncheck the Bottom bottle closure enabled box, set Pressure to Enable Upcast to (0.5 x depth). Pressure Change to Enable upcast is 2. Click on the Bottle Closure Pressures/Times tab and select the Number of Bottles to Close and type the closure pressures.

8.1.3.2 Close on Elapsed Time

Set the Number of bottles using the drop down box, then Bottle Closure Times to allow for time to deploy the CTD and become stationary for each bottle/depth. For very shallow sampling, allow for 3 minutes of CTD equilibration and one minute of casting prior to the first sample. Samples only need to be separated by 0.1 minutes if conducting freps or multiple bottles at one depth. Note that if you use this method, the elapsed time begins when you click the Arm button!

Click on the OK button. Click on the Program Button. Be patient-this takes about 20 seconds to complete. Click on the Arm Button.

8.1.4 Deployment

Cock all bottles on the carousel, tighten all air valves and close each Niskin's spigot. Communicate with the vessel's skipper to determine if deployment is OK. Detach the computer cable from the AFM and attach the dummy plug. Make sure the connection is good and that all air has been "burped out". See section 13 for info on rinsing the TC Duct. Tighten the plastic fitting. Remove the rinsing syringe and slowly slide the CTD on/off switch to the on position. Using the deck crane and a swivel shackle, lift the unit out of the vessel and place in the water so the top of the CTD package is slightly under water.. Adjust the meter wheel. Make sure the elapsed time between switching the unit on and placing

it in the water is less than two minutes. After a total of five minutes from the time the switch was turned on, begin the descent at 0.5 meters per second for the first 20 meters and then 1.5 meters per second below that. (slower rates will produce better data). If necessary, Stop the descent at the proper depth and wait for the period indicated in the Time to Hold Stationary at Bottom setting, otherwise instantly begin the upcast after the proper depth has been achieved. On the upcast, ascend at 1.5 meters per second until the top 20 meters where you slow down to less than 0.5 m/s. .Once the CTD is in sight, inform the skipper and place the CTD on the deck. Immediately turn the on/off switch to off and rinse the TC duct, temperature probe, conductivity cell, DO probe, fluorometer and transmissometer with 10-100 mL of RO water.

8.1.5 Filling Sample Bottles

Following the CTD retrieval, water collected in each Niskin bottle is to be transferred to individual sample bottles as soon as possible. The order of bottle filling should be described in each Sampling and Analysis Plan or Sampling Procedure SOP. Prior to the next cast, the bottles must be cocked and the air vents and spouts closed.

8.1.6 Data Upload

Remove the dummy plug on the AFM bulkhead connector and connect the 10-meter four-pin data I/O cable with the blue label. In the SeaTermAF software, click on the Connect CTD button. Click on the status button to verify there is only one cast. If it is greater than 1, note that value minus one for the cast number and record this in the log book. Click on the Upload button. Note the ncasts value. It should be 1. If not, use that value minus one for the cast number. Type in the cast number (usually 0) and press OK. A header prompt will occur and the following information must be entered:
Ship:
Project:
Station:
Operator:
Comments: - leave this field blank under all circumstances.
Click on OK and a Save As box will display. Enter the cast ID and select the proper directory for the file. Click Save and the file will download. Following the hex file download, click on the Connect AFM button. Click on OK. Click on the Upload button and fill in the header information (again). Click on OK and a Save As box will display. Enter the cast ID (same as hex file name) and select the proper directory for the file. Click Save and the file will download.

8.1.7 Data Evaluation

After each cast, two evaluations are to be completed; a display of the sensors to evaluate data quality and sample bottle depth data should be checked before moving on to a new cast site.

8.1.7.1 Reviewing the Cast Profile

Open the program entitled “Seasave-Win32”. Click on Screen Display and Edit Selected Display Window. Click on Select Display (.DSO) File and select the proper file (salt.dso or fresh.dso). Click on OK.

Click on Modify Display Parameters and enter the proper maximum depth and modify any other parameters that may be appropriate. Click on OK but don’t save the settings since they will remain the same until you close the program.

Click on Archived Data and No Wait. Click on Archived Data and Start. Select the appropriate data (.dat) and instrument configuration (.con) files. Click on the green Start Display button. The cast should be displayed and the operator can evaluate the data quality based on the results. This evaluation is based on experience and an understanding of historical data. The operator should look for signs of instrument anomalies such as spikes, drifts, unexpected noise and significant differences between the downcast and upcast. Also, operators should be familiar with the symptoms of a plugged air vent, hitting the bottom and plugging the TC duct and when a hose becomes detached, stopping the controlled flow of water past the sensors. If any of these problems should be identified, the cast should be discarded and done over.

8.1.7.2 Sample Bottle Depth Data Processing

After the upload, please follow these steps to determine if the Niskins tripped at the proper depth:

On the desktop in Windows, open SBE Data Processing-Win32. Under Run, open Data Conversion. Open the Program setup file DatCnv.psa Select the proper configuration file. Select the input file (the cast that was just previously uploaded with the .hex extension). The output directory should be the

same as the input directory. Output file should be the same as the input files, but without an extension. Click on Start Process. Following processing, click Cancel.

Open Bottle Summary. Open the Program setup file BottleSum.psa.
Select the input file (the .ros file that was created during Data Conversion). Make sure the output directory is the same as the input directory. Name append should be blank. The Output file should be the same as the input files, but with a .btl extension. Click on Start Process and once the program has completed, click on Exit. Close SBE Data Processing.

Open Microsoft Excel and open the appropriate .btl file that was just created. Click Next. Select Space Delimiters (Tab is already selected). Click on finish, then scroll down and look at cell F49, F53, F57, F61, F65, F69, F73, etc to compare the actual sampled depth to the target depth. See section 9.6 for acceptance criteria. Corrective action would include qualifying data in LIMS and filling out a Data Anomaly Form. The DAF is electronically entered into LIMS.

8.1.8 Data Reduction
See section 10.1

8.2 CTD without AFM

8.2.1 Prior to the first cast of the Day
Remove the dummy plug on the AFM bulkhead connector and connect the 10 meter four pin data I/O cable (801616). Connect the opposite end of the I/O cable to the 9 pin serial port on the PC. In Windows, open Open TermAF Click on the Connect CTD Button. An S> prompt should appear. Note the connection is using a baud rate of 4800. Type st and press Enter. This will prompt you for the correct time. Type in the time using the following format; e.g. 134325 is 1:34:25 pm. Press Enter and type the date; e.g. 091006 is September 10, 2006. Press Enter. Click on the Status button. The important things to look for are the vmain (the nicad battery stops working below 7.4 volts), the vlith (this should be >5 and can be replaced only by the factory), the minimum frequency for pump turn on (3500 for salt water, 2000 for fresh water), and the correct time and date. If the main battery voltage is low, replace with either a freshly charged nicad battery or new alkaline batteries (use cc if changing battery types). If the minimum frequency for pump turn on is incorrect, use the cc command to adjust to the correct setting).

8.2.2 Programming CTD
In TermAF, click on the Connect CTD button. If the minimum frequency to turn pump on is incorrect, adjust it according to 8.2.1. At the S> prompt, type il to initialize logging. Click on the Init Log button. This changes the ncast to 0 and prepares the instrument for the upcoming cast. Wait for about 5 seconds until a message box confirms the CTD is ready to go. . .

8.2.3 Deployment
Communicate with the vessel's skipper to determine if deployment is OK. Detach the computer cable from the CTD and attach the dummy plug. Make sure the connection is good and that all air has been "burped out". Tighten the plastic fitting. Remove the rinsing syringe and slowly slide the CTD on/off switch to the on position. Using the deck crane and a swivel shackle, lift the unit out of the vessel and place in the water so the top of the CTD package is slightly under water.. Adjust the meter wheel. Make sure the elapsed time between switching the unit on and placing it in the water is less than two minutes. After a total of five minutes from the time the switch was turned on, begin the descent at 0.5 meters per second for the first 20 meters and then 1.5 meters per second below that. (slower rates will produce better data). If necessary, Stop the descent at the proper depth and wait for the period indicated in the Time to Hold Stationary at Bottom setting, otherwise instantly begin the upcast after the proper depth has been achieved. On the upcast, ascend at 1.5 meters per second until the top 20 meters where you slow down to less than 0.5 m/s. .Once the CTD is in sight, inform the skipper and place the CTD on the deck. Immediately turn the on/off switch to off and rinse the TC duct, temperature probe, conductivity cell, DO probe, fluorometer and transmissometer with RO water.

8.2.4 Data Upload
Remove the dummy plug on the CTD bulkhead connector and connect the 10-meter four-pin data I/O cable with the blue label. In the SeaTermAF software, click on the Connect CTD button. Click on the status button to verify there is only one cast. If it is greater than 1, note that value minus one for the

cast number and record this in the log book. Click on the Upload button. Note the ncasts value. It should be 1. If not, use that value minus one for the cast number. Type in the cast number (usually 0) and press OK. A header prompt will occur and the following information must be entered:
Ship:
Project:
Station:
Operator:
Comments: - leave this field blank under all circumstances.

Click on OK and a Save As box will display. Enter the cast ID and select the proper directory for the file. Click Save and the file will download.

8.2.5 Reviewing the Cast Profile

Open the program entitled "Seasave-Win32". Click on Screen Display and Edit Selected Display Window. Click on Select Display (.DSO) File and select the proper file (salt.dso or fresh.dso). Click on OK.

Click on Modify Display Parameters and enter the proper maximum depth and modify any other parameters that may be appropriate. Click on OK but don't save the settings since they will remain the same until you close the program.

Click on Archived Data and No Wait. Click on Archived Data and Start. Select the appropriate data (.dat) and instrument configuration (.con) files. Click on the green Start Display button. The cast should be displayed and the operator can evaluate the data quality based on the results. This evaluation is based on experience and an understanding of historical data. The operator should look for signs of instrument anomalies such as spikes, drifts, unexpected noise and significant differences between the downcast and upcast. Also, operators should be familiar with the symptoms of a plugged air vent, hitting the bottom and plugging the TC duct and when a hose becomes betached, stopping the controlled flow of water past the sensors. If any of these problems should be identified, the cast should be discarded and done over..

8.2.6 Data Reduction

See section 10.1

8.3DataLogger (Surface Light Intensity)

8.3.1Preparation for Deployment: Programming the LI-1400

Connect the sensor to the BNC setting I1. Press the On/Off button. Press the Fct button. Arrow to the right until Clear Memory appears. Press Enter. Arrow down until the display reads !Clear Mem ?NO!. Arrow right and the NO will change to YES. Press Enter and the memory will clear.

Press the Setup button and the arrow right button until SETUP LOGGING is on the screen. Press Enter. Arrow down until the cursor is on LR1. Press Enter. Type in the start time in military time and press Enter. Arrow down and type the Stop Time. Press Enter. Arrow down and type in the Smpl Per= and arrow to the right or left to choose different sampling times. Currently we are using 1 second. Arrow down to Log Per= and arrow to the right or left to choose different logging times. We are currently using 30 seconds. Press Esc. Arrow up until the cursor is under Logging=Off. Press the right arrow button for Logging=On. Monitor the new data by pressing the View button and arrowing to the right or left to choose VIEW NEW DATA. Press Enter and current Light Intensity data will appear on the screen. If sampling for more than 15 minutes, the display will turn off automatically, but logging will continue until the sampling period is over. The instrument uses an AC adapter and four alkaline "AA" batteries with a life of approximately 50 hours for backup.

8.3.2 Licor Data Upload

The LI-1400 utilizes a Microsoft Windows software package. Connect the LI-1400's RS-232 port to the PC's COM1 port using a 9 pin serial cable. Open the LI-1400 software package. Open the Liberty.I14 file and click on Remote, Connect. Select Channels I1, click on Remote, then Receive data. Select the 'all' button and click on OK. Type file name (using the following format: YYMMDDpar.txt, where YY is year, MM is month and DD is date) and press Enter. At this point, the logged data will upload to the PC. When it is finished, close the LI-1400 software and open the text file with Microsoft Excel.

9.0 QA/QC REQUIREMENTS

9.1 Calibration

Calibration of the Thermometer, Conductivity, and Dissolved Oxygen sensors will be calibrated at Seabird on an annual basis. The SBE-43 Dissolved Oxygen sensor is post-calibrated using comparisons to Winkler DO samples. The C-Star Transmissometer is also post-calibrated in the lab.. This is done post-cruise for two reasons. One is to determine if the instrument has drifted since the last calibration and secondly, there is no other way to determine if the results are within a reasonable range since there are no conventional chemistry tests or field tests that can be done for evaluation. There are no standards to do a "check", so post-cruise calibrations are the most efficient and sensible method. The PAR sensors are sent to Li-Cor on a bi-annual basis while the C-Star Transmissometer and the Wetstar Fluorometer are sent to Wetlabs annually. The depth sensor is maintained and calibrated by Seabird every 5 years based on their recommendation.

9.1.1 SBE 43 Post-Cruise Calibration for Dissolved Oxygen

9.1.1.1 Initial DO evaluation: Using the method in section 8.1.7.2, process CTD bottle data using the LIMS datcnv.psa file and the previous month's configuration file to calculate the pre-cal CTD dissolved oxygen values. Note these values on a copy of the Conventional Chemistry Unit's Winkler analysis form for the associated samples. This will give the operator a general idea of how much the instrument has drifted since the last calibration and the general quality of the data. There are no acceptance windows, but if the differences between the Winklers and the CTD DO are greater than 1 mg/L, the instrument should be sent in for repair.

9.1.1.2 Seabird 64-2 Regression: Reprocess the CTD bottle data using datcnv cal 43.psa and the previous month's configuration file to obtain the following data: Pressure (db), Temperature (deg. C), Salinity (PSS), Oxygen Saturation (ml/l) and SBE 43 Output Voltage. Enter these values into the SBE43 DO Calibration Template (taken from Seabird's Application Note 64-2 Regression), along with the Conventional Chemistry Unit's Winkler values to calculate new SOC and Voffset values. Do not use the FREP samples in the SOC and BOC calculation. These samples will be used to evaluate the quality of the Winkler vs. CTD data.

9.1.1.3 Updating the configuration file: Enter the new SOC and Voffset values into a new configuration file with appropriate nomenclature. This configuration file is now ready to be used to reprocess the new LIMS Bottle data and the CTD database data.

9.1.1.4 Compare the final calculated Bottle Data DO values to the Winkler values for a final quality evaluation. Control windows have not been set for qualification.

9.1.2 C-Star Post-Cruise Calibration for Light Transmission

Using the C-Star Calibration Sheet, calibrate the C-Star by monitoring voltages with no blockage followed by complete blockage. This is done by first cleaning the lenses with RO water and alcohol using Kim Wipes. Disconnect the AFM-CTD cable and insert the 10 meter four pin data I/O cable (801616). Connect the opposite end of the I/O cable to the 9 pin serial port on the PC. Open TermAF, click on the Connect CTD button. Change the minimum frequency to turn pump on to 3500 using the method in 8.2.1. Following this, at the S> prompt type il to initialize logging. Click on the Init Log button. This changes the ncast to 0 and prepares the instrument for the upcoming cast. Wait for about 5 seconds until a message box confirms the CTD is ready to go. Open Seasave-Win32. Open the C-StarTransmissometer Seasave Configuration. Click on RealTimeData and Start Acquisition. Select the previous month's configuration file and uncheck Store on Disk. Make sure the COMM port configuration settings are COM1 and baud rate of 4800. Click on Start Acquire and begin monitoring the voltages. After approximately 200 scans or when the Light Transmission values become stable begin reporting the following: Scan #, CTD Temp, Volt 1, and Light %. Completely block the light pathway and record the values as "Blocked" on the calibration sheet. Compute the M and B values and enter them into the new CTD configuration file.

9.2 Replicate Measurements

Replicate sensor readings will be reported to LIMS once per cruise. . Both the original and replicate samples are true samples and loaded to LIMS. In order to calculate RPD values, QC replicate samples are created in LIMS using the FREP locator and linked back to the original sample. See the table below for acceptable limits.

Parameter	DO, Field	Sal, Field	Samp Depth	Sample Temp	Light Transmission, Field
Acceptance Limits	20 % RPD	0.3 PSS	1 or 4 meters	0.3 deg C	20 % RPD

9.3 Split Samples and Field Replicates

For marine projects, Salinity and Dissolved Oxygen measurements will be analyzed synoptically using water samples in the Conventionals Unit. The frequency will be a minimum of 1 per cast to facilitate the dissolved oxygen post-cruise calibration. The acceptance range for field dissolved oxygen versus Winkler DO is 20% RPD. For salinity, the acceptance range is 0.3 PSS. Field replicates are analyzed at a minimum frequency of 1 per 20 samples or once per day, whichever is more frequent.

9.4 Method Blanks

Method Blanks are not appropriate for CTD analysis.

9.5 Continuing Calibration Verification

CCV's are not appropriate for CTD analysis.

9.6 Depth Comparison

Following the Bottle Summary calculations, each bottle trip will be compared with the intended sample depths. For samples less than 100 meters, the intended depth and the CTD depth should be within 1 meter. For depths greater than 100 meters, the difference should be no greater than 4 meters.

10.0 DATA REDUCTION, REPORTING, REVIEW AND DOCUMENTATION

10.1 LIMS

10.1.1 Data Entry to LIMS

After all post-calibration work and creation of a workgroup with the appropriate sample numbers and products, follow the steps in 8.1.7.2 to create the necessary .btl files required to extract the LIMS data. Open Excel, Click on EnvLab then ESS Data Entry. Click on the CTD Data option button then Open Data. Find the .btl file, select it and click OK. The macro will run and a pop-up window will ask you to Enter Sample Numbers, Surface PAR data, and then press Load to LIMS button. Click on OK. Complete these tasks and other necessary editing. Click on the Post to LIMS button. It will then ask you if you are ready to post and say Yes. The data will automatically be transferred to LIMS. Note that the values for all LIMS parameters, including sample depth, will be averaged for three seconds during the bottle trip period. Field replicates will then need to be created in Workstat and those data will be entered into LIMS electronically.

10.1.2 LIMS Data Review

Seedpak3 reports are to be reviewed against the *.xls rossum files for accuracy. Following this, the data is approved and moved to EDS. Once all the laboratory analyses have been completed, an EDS report is created to compare the CTD data versus the laboratory data.

10.1.3 Documentation and Data Reporting

Seedpak3 reports, *.txt transfer files, *.xls rossum files, post-cruise calibration records and lab data comparisons are to be filed as a hard copy report. All electronic files are stored and backed up on a daily basis. Instrument calibration records done by the manufacturer, including sensor serial numbers and inclusive dates, are stored in a logbook and updated when applicable.

10.1.4 LIMS Table

Product	Parameter	Listtype	Units	MDL	RDL	Sigfig MDL	Sigfig RDL
SAMP DEPTH	Sample Depth	ESS-CTD	m	n/a	n/a	2	3

SAMP TEMP	Sample Temperature, Field	ESS-CTD	Deg. C	n/a	n/a	*	*
DO, FIELD	Dissolved Oxygen, Field	ESS-CTD	mg/L	0.5	1.0	2	3
SAL, FIELD	Salinity, Field	ESS-CTD	PSS	n/a	n/a	5	5
DENSITY, FIELD	Density, Field	ESS-CTD	kg/m^3	n/a	n/a	7	7
CHLA, FIELD	Chlorophyll	ESS-CTD	ug/L	0.06	0.12	2	3
LIGHT TRANSMISSION	Light Transmission	ESS-CTD	% light	0.01	0.01	2	3
PAR, FIELD	Light Intensity (PAR), Field	ESS-CTD	$umol/sm^2$	n/a	n/a	*	n/a
PAR, SURF, FIELD	Surface Light Intensity (PAR), Field	ESS-FM	$umol/sm^2$	n/a	n/a	*	*

*= Round to 0.1

10.2 Full Cast File Handling

Follow the instructions in the CTD File Handling Protocol (2.5). Completed data files are reviewed, qualified and loaded to the CTD database.

11.0 STANDARDS AND REAGENTS

11.1 Triton X100 cleansing solution: Add 10 ml of solution to 1 liter of RO water. Prepare fresh monthly. Use this reagent very sparingly and rinse extremely thoroughly with RO water following the use. It can foul the dissolved oxygen membrane.

11.2 RO Water: Reverse-osmosis water produced at the laboratory and retrieved from an RO water tap. This reagent can be disposed of down the drain or overboard. ASTM Type I or equivalent. It is stored in a 2 liter HDPE bottle and replaced monthly.

11.3 **Alkali-Iodide-Azide (AIA)-** AIA is a poisonous and caustic reagent used for Winkler dissolved oxygen fixation. Contact with skin must be avoided. AIA must stored in a well ventilated, dry, and cool area. Working reagents will be stored in a re-pipet dispenser. Always wear gloves and goggles when working with AIA. AIA is purchased by the Conventional Chemistry Unit and dispensed by a small re-pipet dispenser on the Liberty.

11.4 **Manganous Sulfate (MnS04). A reagent used for Winkler dissolved oxygen fixation. Avoid contact with skin. Store in a well ventilated, dry and cool area in a re-pipet dispenser. Always wear gloves and safety glasses when working with MnSO4. MnSO4 is purchased by the Conventional Chemistry Unit and dispensed by a small re-pipet dispenser on the Liberty.**

12.0 CONTAMINATION

Oil and grease can coat sensors and hoses and can destroy the on-line pump. Airborne contaminants can affect conductivity results if allowed to enter and dry in cell. Any material capable of fluorescing at or near 676 nm can affect the chlorophyll analysis. In addition, high turbidity may create a high bias with respect to chlorophyll values. Particles caught in the inverted ‘Y’ fitting can stop air from exiting, thus not allowing the pump to prime or causing poor readings throughout the instrument. Dirty transmissometer lenses can reduce light transmission values.

13.0 PREVENTATIVE MAINTENANCE

The TC duct, temperature probe, conductivity cell, DO probe, and fluorometer must be rinsed with RO water prior to and immediately following each cast. Rinse with a full 60cc syringe and a connecting tube (7/16” Tygon) on the end of the TC duct. All other parts of the CTD and carousel must be rinsed thoroughly with fresh water following each cruise. Store the CTD with the conductivity cell full of RO water between cruises. Use a 1% TritonX soution to clean the sensors if oil or grease has been encountered. Rinse thoroughly with RO water following the Triton cleaning. Use a dilute sodium hypochlorite solution (1% bleach) to kill biological growth if absolutely necessary. Rinse immediately with RO water (5 minutes minimum) following the bleach cleaning.

For storage, The DO cell should remain free of water, but the high humidity from the RO water in the conductivity cell will keep the DO sensor fresh.

The DO sensor membrane should be replaced at least every year by Seabird. Clean the transmissometer lenses with alcohol, RO water and Kim Wipes before and after each cruise. Maintenance must be recorded in the maintenance logbook.

14.0 TRAINING

New analysts must successfully perform maintenance, field measurements and data reduction/review under the direct supervision of an experienced analyst following review of this document.

15.0 REFERENCES

SBE 25 Sealogger CTD Operating Manual
CTD Data Acquisition software: Seasoft
Model LI-1400 Datalogger Instruction Manual
Li-Cor Surface PAR Data Acquisition software: LI-1400.

16.0 APPENDIX

King County Environmental Lab CTD File Handling Protocol

Datcnv
- Process scans until end of file
- Scans to skip over = 1100
- Use ascii output
- Convert Data from Upcast and Downcast
- Create converted (.CNV) file only
- Output Variables (in this order) = scan count, pressure (strain gauge db), depth (salt water,meters), temperature ITS-90, conductivity (S/m), oxygen voltage (SBE 43), PAR/irradiance biospheric Licor, Fluroescence (wetlab wetstar mg/m3), Beam Transmission (Chelsea/Seatech/Wetlab).
- Do not output water bottle data, this will be done by the environmental laboratory and stored on LIMS for later retrieval.
- Creates a file with the same name and a .cnv file extension.

Alignctd
Advance Values
- Primary Conductivity alignment = 0.11 seconds
- Oxygen alignment = 2.0 seconds
- Fluorescence alignment = 4.0 seconds
- Everything else = 0
- Overwrite .cnv file

Cell Thermal Mass
- Alpha = 0.04
- 1/beta = 8.0
- Corrects for cell thermal mass
- Overwrite .cnv file

Derive
- Variables to be Derived = salinity, oxygen mg/L, potential temperature, density kg/m3, sigma-theta, descent rate.
- Variable Coefficients (oxygen, descent rate) = 2 seconds (for both coefficients)
- Overwrite .cnv file

Binavg
- Arrange into depth bins, no interpolation
- Bins are 0.5 meters in size
- Include number of scans per bin in output file
- Exclude bad scans (marked with Loopedit)
- Skip 0 scans
- Process upcast and downcast
- Don’t include surface bin
- Overwrite new .cnv file

Appendix F

Axys Analytical PCB analysis SOP

Summary of AXYS Method MLA-010 Rev 10:

ANALYTICAL METHOD FOR THE DETERMINATION OF:

209 PCB CONGENERS BY EPA METHOD 1668A[1] OR

EPA METHOD CBC01.2[2]

AXYS Method MLA-010 describes the analysis for the determination of the concentration of 209 PCB congeners in sediment, soil, sludge, tissue (including blood), aqueous samples, milk, solvent extracts, air samples and XAD columns.

Target Analytes

This analytical method determines the concentrations of all 209 PCB congeners by high resolution GC/MS (HRGC/HRMS). For EPA Method 1668A applications PCBs are reported using the congener numbering convention used in Method 1668A, for EPA Method CBC01.2 applications PCBs are reported using the congener numbering convention in EPA Method 1668B.

The concentrations of some PCB congeners are reported as the sum of two or more congeners due to coelution of the congeners. The coeluting congeners are listed below.

COELUTING PCB CONGENERS	
PCB 12, 13	PCB 93, 95, 98, 100, 102
PCB 30/18	PCB 107, 124
PCB 20, 28	PCB 110, 115
PCB 21, 33	PCB 128, 166
PCB 26, 29	PCB 129, 138, 160, 163
PCB 40, 41, 71	PCB 134, 143
PCB 44, 47, 65	PCB 135, 151, 154
PCB 45, 51	PCB 139, 140
PCB 49, 69	PCB 147, 149
PCB 50, 53	PCB 156, 157[1]
PCB 59, 62, 75	PCB 153, 168
PCB 61, 70, 74, 76	PCB 171, 173
PCB 83, 99	PCB 183/185
PCB 85, 116, 117	PCB 180, 193
PCB 86, 87, 97 108, 119, 125	PCB 197/200
PCB 88, 91	PCB 198, 199
PCB 90, 101, 113	

[1] A second GC/MS analysis on a DB-1 column (30 m, 0.25 mm I.D., 0.25 µm film thickness) resolves the PCB 156/157 coeluting pair. This second analysis is performed upon request by the client.

The concentrations of all other PCB congeners are reported as the concentration of individual congeners.

A subset of congeners designated as “toxic” by the World Health Organization, can be reported with the associated toxic equivalents.

WHO TOXIC PCB CONGENERS	CONGENER NUMBER
3,4,4’,5-Tetrachlorobiphenyl (TeCB)	81
3,3',4,4'-TCB	77
2,3,3',4,4'-Pentachlorobiphenyl (PeCB)	105
2,3,4,4',5-PeCB	114
2,3',4,4',5-PeCB	118
2',3,4,4',5-PeCB	123
3,3',4,4',5-PeCB	126
2,3,3',4,4',5-Hexachlorobiphenyl (HxCB)	156
2,3,3',4,4',5'-HxCB	157
2,3',4,4',5,5'-HxCB	167
3,3',4,4',5,5'-HxCB	169
2,3,3',4,4',5,5'-HpCB	189

Upon client request, any subset of the 209 PCB congeners may be reported.

EXTRACTION

All samples are spiked with ^{13}C-labelled surrogate standards prior to extraction and extracted as per the table below. Optional extraction procedures are shown within parentheses.

Sample Extraction

Matrix	Extraction
Aqueous	<1% solids Liquid-liquid extraction with dichloromethane. >1% solids sample is filtered prior to extraction and the particulate fraction separately extracted by Soxhlet extraction with dichloromethane. The filtrate is liquid-liquid extracted with di-chloromethane. The two extracts are then combined.
Solid (sediment, soil, sludge, particles on filter paper)	Soxhlet extraction with dichloromethane (optional: Dean-Stark Soxhlet extraction with toluene)
Tissue	Soxhlet extraction with dichloromethane (optional: Base digestion and liquid-liquid extraction with hexane)
Whole blood/serum	Liquid-liquid extraction with ethanol:hexane:saturated ammonium sulphate.
Milk	Liquid-liquid extraction with acetone and hexane.

XAD-2 column and filter	XAD-2 adsorbent is dried and extracted by Soxhlet with dichloromethane (optional Dean-Stark Soxhlet with toluene extraction). The filter is extracted by Dean-Stark Soxhlet extraction using toluene.
Ambient air (PUF and filter)	The PUF and filter(s) are Soxhlet extracted together using dichloromethane
Stationary Source Air Samples (Stack Gas sample trains)	The filter is sonicated with dilute hydrochloride acid and filtered. Equipment rinsates are collected, filtered, dried and/or extracted depending on sampling conditions.

COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up using the following chromatography columns:

- Multi-layered Acid/Base Silica
- Florisil
- Alumina

Extracts may be cleaned up using some or all of the following procedures as necessary:

- column chromatography on Biobeads
- column chromatography on 4.5% carbon/Celite

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed on a SPB-Octyl column coupled to a high-resolution mass spectrometer (HRMS). The HRMS is operated at 8000 mass resolution throughout the mass range and 10000 for the center mass in each retention time window in the voltage selected ion-recording mode (V-SIR). Selected PFK ions are used as a reference for mass lock. Two masses from the molecular ion cluster are used to monitor each of the target analytes and ^{13}C-labelled surrogate standards.

Upon client request resolution of the PCB 156/157 co-elution is achieved using a DB-1 chromatography column.

Analysis of the extract on either a DB-1 or DB-5 column is useful to resolve potential interferences with PCB 169 (from PCB 190).

Table 6a. Nomenclature for EPA 1668A Applications

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
2 - MoCB	1	2051-60-7		11:34:00	1L	11:34:00	1.000	-1,3	0.999	1.004
3 - MoCB	2	2051-61-8		13:38:00	3L	13:48:00	0.988	6	0.984	0.992
4 - MoCB	3	2051-62-9		13:49:00	3L	13:48:00	1.001	-1,3	0.999	1.004
22' - DiCB	4	13029-08-8		14:04:00	4L	14:03:00	1.001	-1,3	0.999	1.004
26 - DiCB	10	33146-45-1		14:14:00	4L	14:03:00	1.013	6	1.009	1.017
25 - DiCB	9	34883-39-1		16:06:00	4L	14:03:00	1.146	6	1.142	1.149
24 - DiCB	7	33284-50-3		16:16:00	4L	14:03:00	1.158	6	1.154	1.161
23' - DiCB	6	25569-80-6		16:31:00	4L	14:03:00	1.176	6	1.172	1.179
23 - DiCB	5	16605-91-7		16:49:00	4L	14:03:00	1.197	6	1.193	1.200
24' - DiCB	8	34883-43-7		16:58:00	4L	14:03:00	1.208	6	1.204	1.211
35 - DiCB	14	34883-41-5		18:39:00	15L	20:08:00	0.926	6	0.924	0.929
33' - DiCB	11	2050-67-1		19:32:00	15L	20:08:00	0.970	6	0.968	0.973
34' - DiCB	13	2974-90-5	12 + 13							
34 - DiCB	12	2974-92-7	12 + 13	19:51:00	15L	20:08:00	0.986	6	0.983	0.988
44' - DiCB	15	2050-68-2		20:09:00	15L	20:08:00	1.001	-1,3	0.999	1.002
22'6 - TriCB	19	38444-73-4		17:15:00	19L	17:13:00	1.002	-1,3	0.999	1.003
246 - TriCB	30	35693-92-6	18 + 30							
22'5 - TriCB	18	37680-65-2	18 + 30	19:09:00	19L	17:13:00	1.112	6	1.109	1.115
22'4 - TriCB	17	37680-66-3		19:36:00	19L	17:13:00	1.138	6	1.136	1.141
23'6 - TriCB	27	38444-76-7		19:50:00	19L	17:13:00	1.152	6	1.149	1.155
236 - TriCB	24	55702-45-9		19:58:00	19L	17:13:00	1.160	6	1.157	1.163
22'3 - TriCB	16	38444-78-9		20:05:00	19L	17:13:00	1.167	6	1.164	1.169
24'6 - TriCB	32	38444-77-8		20:37:00	19L	17:13:00	1.197	6	1.195	1.200
2'35 - TriCB	34	37680-68-5		21:56:00	19L	17:13:00	1.274	6	1.271	1.277
235 - TriCB	23	55720-44-0		22:06:00	19L	17:13:00	1.284	6	1.281	1.287
245 - TriCB	29	15862-07-4	26 + 29							
23'5 - TriCB	26	38444-81-4	26 + 29	22:26:00	19L	17:13:00	1.303	10	1.298	1.308
23'4 - TriCB	25	55712-37-3		22:40:00	37L	27:27:00	0.826	6	0.824	0.828
24'5 - TriCB	31	16606-02-3		22:59:00	37L	27:27:00	0.837	6	0.835	0.839
244' - TriCB	28	7012-37-5	20 + 28							

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233' - TriCB	20	38444-84-7	20 + 28	23:18:00	37L	27:27:00	0.849	10	0.846	0.852
234 - TriCB	21	55702-46-0	21 + 33	23:30:00	37L	27:27:00	0.856	10	0.853	0.859
2'34 - TriCB	33	38444-86-9	21 + 33							
234' - TriCB	22	38444-85-8		23:57:00	37L	27:27:00	0.872	6	0.871	0.874
33'5 - TriCB	36	38444-87-0		25:35:00	37L	27:27:00	0.932	6	0.930	0.934
34'5 - TriCB	39	38444-88-1		25:58:00	37L	27:27:00	0.946	6	0.944	0.948
345 - TriCB	38	53555-66-1		26:33:00	37L	27:27:00	0.967	6	0.965	0.969
33'4 - TriCB	35	37680-69-6		27:03:00	37L	27:27:00	0.985	6	0.984	0.987
344' - TriCB	37	38444-90-5		27:28:00	37L	27:27:00	1.001	-1,3	0.999	1.002
22'66' - TeCB	54	15968-05-5		20:25:00	54L	20:25:00	1.000	-1,3	0.999	1.002
22'46 - TeCB	50	62796-65-0	50 + 53	22:41:00	54L	20:25:00	1.111	10	1.107	1.115
22'56' - TeCB	53	41464-41-9	50 + 53							
22'36 - TeCB	45	70362-45-7	45 + 51	23:24:00	54L	20:25:00	1.146	10	1.142	1.150
22'46' - TeCB	51	68194-04-7	45 + 51							
22'36' - TeCB	46	41464-47-5		23:41:00	54L	20:25:00	1.160	6	1.158	1.162
22'55' - TeCB	52	35693-99-3		25:11:00	54L	20:25:00	1.233	6	1.231	1.236
23'5'6 - TeCB	73	74338-23-1		25:20:00	54L	20:25:00	1.241	6	1.238	1.243
22'35 - TeCB	43	70362-46-8		25:26:00	54L	20:25:00	1.246	6	1.243	1.248
23'46 - TeCB	69	60233-24-1	49 + 69							
22'45' - TeCB	49	41464-40-8	49 + 69	25:40:00	54L	20:25:00	1.257	10	1.253	1.261
22'45 - TeCB	48	70362-47-9		25:59:00	54L	20:25:00	1.273	6	1.270	1.275
2356 - TeCB	65	33284-54-7	44 + 47 + 65							
22'44' - TeCB	47	2437-79-8	44 + 47 + 65							
22'35' - TeCB	44	41464-39-5	44 + 47 + 65	26:14:00	54L	20:25:00	1.285	10	1.281	1.289
2346 - TeCB	62	54230-22-7	59 + 62 + 75							
244'6 - TeCB	75	32598-12-2	59 + 62 + 75							
233'6 - TeCB	59	74472-33-6	59 + 62 + 75	26:34:00	54L	20:25:00	1.301	10	1.297	1.305
22'34' - TeCB	42	36559-22-5		26:45:00	54L	20:25:00	1.310	6	1.308	1.313
22'34 - TeCB	41	52663-59-9	40 + 41 + 71							
23'4'6 - TeCB	71	41464-46-4	40 + 41 + 71							
22'33' - TeCB	40	38444-93-8	40 + 41 + 71	27:14:00	54L	20:25:00	1.334	10	1.330	1.338
234'6 - TeCB	64	52663-58-8		27:31:00	54L	20:25:00	1.348	6	1.345	1.350
23'55' - TeCB	72	41464-42-0		28:24:00	81L	34:31:00	0.823	6	0.821	0.824

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
23'45' - TeCB	68	73575-52-7		28:42:00	81L	34:31:00	0.831	6	0.830	0.833
233'5 - TeCB	57	70424-67-8		29:09:00	81L	34:31:00	0.845	6	0.843	0.846
233'5' - TeCB	58	41464-49-7		29:23:00	81L	34:31:00	0.851	6	0.850	0.853
23'45 - TeCB	67	73575-53-8		29:34:00	81L	34:31:00	0.857	6	0.855	0.858
234'5 - TeCB	63	74472-34-7		29:50:00	81L	34:31:00	0.864	6	0.863	0.866
2345 - TeCB	61	33284-53-6	61 + 70 + 74 + 76	30:11:00	81L	34:31:00	0.874	12	0.872	0.877
23'4'5 - TeCB	70	32598-11-1	61 + 70 + 74 + 76							
2'345 - TeCB	76	70362-48-0	61 + 70 + 74 + 76							
244'5 - TeCB	74	32690-93-0	61 + 70 + 74 + 76							
23'44' - TeCB	66	32598-10-0		30:32:00	81L	34:31:00	0.885	6	0.883	0.886
233'4 - TeCB	55	74338-24-2		30:41:00	81L	34:31:00	0.889	6	0.887	0.890
233'4' - TeCB	56	41464-43-1		31:13:00	81L	34:31:00	0.904	6	0.903	0.906
2344' - TeCB	60	33025-41-1		31:27:00	81L	34:31:00	0.911	6	0.910	0.913
33'55' - TeCB	80	33284-52-5		31:54:00	81L	34:31:00	0.924	6	0.923	0.926
33'45' - TeCB	79	41464-48-6		33:29:00	81L	34:31:00	0.970	6	0.969	0.972
33'45 - TeCB	78	70362-49-1		34:05:00	81L	34:31:00	0.987	6	0.986	0.989
344'5 - TeCB	81	70362-50-4		34:32:00	81L	34:31:00	1.000	-1,3	1.000	1.001
33'44' - TeCB	77	32598-13-3		35:08:00	77L	35:07:00	1.000	-1,3	1.000	1.001
22'466' - PeCB	104	56558-16-8		26:10:00	104L	26:08:00	1.001	-1,3	0.999	1.002
22'366' - PeCB	96	73575-54-9		26:32:00	104L	26:08:00	1.015	10	1.012	1.018
22'45'6 - PeCB	103	60145-21-3		28:34:00	104L	26:08:00	1.093	6	1.091	1.095
22'356' - PeCB	94	73575-55-0		28:48:00	104L	26:08:00	1.102	6	1.100	1.104
22'35'6 - PeCB	95	38379-99-6	93 + 95 + 98 + 100 + 102							
22'44'6 - PeCB	100	39485-83-1	93 + 95 + 98 + 100 + 102							
22'356 - PeCB	93	73575-56-1	93 + 95 + 98 + 100 + 102	29:31:00	104L	26:08:00	1.129	20	1.123	1.136
22'456' - PeCB	102	68194-06-9	93 + 95 + 98 + 100 + 102							
22'3'46 - PeCB	98	60233-25-2	93 + 95 + 98 + 100 + 102							
22'346 - PeCB	88	55215-17-3	88 + 91	30:07:00	104L	26:08:00	1.152	12	1.149	1.156
22'34'6 - PeCB	91	68194-05-8	88 + 91							
22'33'6 - PeCB	84	52663-60-2		30:23:00	104L	26:08:00	1.163	6	1.161	1.165
22'346' - PeCB	89	73575-57-2		30:53:00	104L	26:08:00	1.182	6	1.180	1.184
23'45'6 - PeCB	121	56558-18-0		31:20:00	104L	26:08:00	1.199	6	1.197	1.201
22'355' - PeCB	92	52663-61-3		31:44:00	123L	37:12:00	0.853	6	0.852	0.854

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'5'6 - PeCB	113	68194-10-5	90 + 101 + 113							
22'34'5 - PeCB	90	68194-07-0	90 + 101 + 113	32:19:00	123L	37:12:00	0.869	10	0.866	0.871
22'455' - PeCB	101	37680-73-2	90 + 101 + 113							
22'33'5 - PeCB	83	60145-20-2	83 + 99	32:53:00	123L	37:12:00	0.884	12	0.881	0.887
22'44'5 - PeCB	99	38380-01-7	83 + 99							
233'56 - PeCB	112	74472-36-9		33:04:00	123L	37:12:00	0.889	6	0.888	0.890
23'44'6 - PeCB	119	56558-17-9	86 + 87 + 97 + 108 + 119 + 125							
233'45' - PeCB	108	70362-41-3	86 + 87 + 97 + 108 + 119 + 125							
22'345 - PeCB	86	55312-69-1	86 + 87 + 97 + 108 + 119 + 125	33:29:00	123L	37:12:00	0.900	16	0.897	0.904
22'3'45 - PeCB	97	41464-51-1	86 + 87 + 97 + 108 + 119 + 125							
2'3456' - PeCB	125	74472-39-2	86 + 87 + 97 + 108 + 119 + 125							
22'345' - PeCB	87	38380-02-8	86 + 87 + 97 + 108 + 119 + 125							
234'56 - PeCB	117	68194-11-6	85 + 116 + 117							
23456 - PeCB	116	18259-05-7	85 + 116 + 117							
22'344' - PeCB	85	65510-45-4	85 + 116 + 117	34:12:00	123L	37:12:00	0.919	12	0.917	0.922
233'4'6 - PeCB	110	38380-03-9	110 + 115	34:27:00	123L	37:12:00	0.926	10	0.924	0.928
2344'6 - PeCB	115	74472-38-1	110 + 115							
22'33'4 - PeCB	82	52663-62-4		34:43:00	123L	37:12:00	0.933	6	0.932	0.935
233'55' - PeCB	111	39635-32-0		35:10:00	123L	37:12:00	0.945	6	0.944	0.947
23'455' - PeCB	120	68194-12-7		35:38:00	123L	37:12:00	0.958	6	0.957	0.959
233'4'5 - PeCB	107	70424-68-9	107 + 124	36:50:00	123L	37:12:00	0.990	10	0.988	0.992
2'3455' - PeCB	124	70424-70-3	107 + 124							
233'46 - PeCB	109	74472-35-8		37:05:00	123L	37:12:00	0.997	6	0.996	0.998
2'344'5 - PeCB	123	65510-44-3		37:13:00	123L	37:12:00	1.000	-1,3	1.000	1.001
233'45 - PeCB	106	70424-69-0		37:21:00	123L	37:12:00	1.004	6	1.003	1.005
23'44'5 - PeCB	118	31508-00-6		37:34:00	118L	37:32:00	1.001	-1,3	1.000	1.002
2'33'45 - PeCB	122	76842-07-4		37:55:00	118L	37:32:00	1.010	6	1.009	1.012
2344'5 - PeCB	114	74472-37-0		38:07:00	114L	38:06:00	1.000	-1,3	1.000	1.001
233'44' - PeCB	105	32598-14-4		38:48:00	105L	38:46:00	1.001	-1,3	0.999	1.001
33'455' - PeCB	127	39635-33-1		40:21:00	105L	38:46:00	1.041	6	1.040	1.042
33'44'5 - PeCB	126	57465-28-8		42:02:00	126L	42:01:00	1.000	-1,3	1.000	1.001
22'44'66' - HxCB	155	33979-03-2		32:06:00	155L	32:05:00	1.001	-1,3	0.999	1.002
22'3566' - HxCB	152	68194-09-2		32:17:00	155L	32:05:00	1.006	6	1.005	1.008

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
22'34'66' - HxCB	150	68194-08-1		32:28:00	155L	32:05:00	1.012	6	1.010	1.014
22'33'66' - HxCB	136	38411-22-2		32:51:00	155L	32:05:00	1.024	6	1.022	1.025
22'3466' - HxCB	145	74472-40-5		33:10:00	155L	32:05:00	1.034	6	1.032	1.035
22'34'56' - HxCB	148	74472-41-6		34:45:00	155L	32:05:00	1.083	6	1.082	1.085
22'355'6 - HxCB	151	52663-63-5	135 + 151 + 154							
22'33'56' - HxCB	135	52744-13-5	135 + 151 + 154	35:29:00	155L	32:05:00	1.106	10	1.103	1.109
22'44'5'6 - HxCB	154	60145-22-4	135 + 151 + 154							
22'345'6 - HxCB	144	68194-14-9		35:57:00	155L	32:05:00	1.121	6	1.119	1.122
22'34'56 - HxCB	147	68194-13-8	147 + 149	36:20:00	155L	32:05:00	1.132	10	1.130	1.135
22'34'5'6 - HxCB	149	38380-04-0	147 + 149							
22'33'56 - HxCB	134	52704-70-8	134 + 143	36:36:00	155L	32:05:00	1.141	10	1.138	1.143
22'3456' - HxCB	143	68194-15-0	134 + 143							
22'344'6 - HxCB	139	56030-56-9	139 + 140	36:58:00	155L	32:05:00	1.152	10	1.150	1.155
22'344'6' - HxCB	140	59291-64-4	139 + 140							
22'33'46 - HxCB	131	61798-70-7		37:11:00	155L	32:05:00	1.159	6	1.157	1.161
22'3456 - HxCB	142	41411-61-4		37:20:00	155L	32:05:00	1.164	6	1.162	1.165
22'33'46' - HxCB	132	38380-05-1		37:39:00	155L	32:05:00	1.174	10	1.171	1.176
22'33'55' - HxCB	133	35694-04-3		38:11:00	155L	32:05:00	1.190	6	1.189	1.192
233'55'6 - HxCB	165	74472-46-1		38:37:00	167L	43:57:00	0.879	6	0.878	0.880
22'34'55' - HxCB	146	51908-16-8		38:52:00	167L	43:57:00	0.884	6	0.883	0.885
233'45'6 - HxCB	161	74472-43-8		39:01:00	167L	43:57:00	0.888	6	0.887	0.889
22'44'55' - HxCB	153	35065-27-1	153 + 168	39:32:00	167L	43:57:00	0.900	10	0.898	0.901
23'44'5'6 - HxCB	168	59291-65-5	153 + 168							
22'3455' - HxCB	141	52712-04-6		39:43:00	167L	43:57:00	0.904	6	0.903	0.905
22'33'45' - HxCB	130	52663-66-8		40:08:00	167L	43:57:00	0.913	6	0.912	0.914
22'344'5 - HxCB	137	35694-06-5		40:22:00	167L	43:57:00	0.918	6	0.917	0.920
233'4'5'6 - HxCB	164	74472-45-0		40:29:00	167L	43:57:00	0.921	6	0.920	0.922
22'344'5' - HxCB	138	35065-28-2	129 + 138 + 160 + 163							
233'4'56 - HxCB	163	74472-44-9	129 + 138 + 160 + 163							
22'33'45 - HxCB	129	55215-18-4	129 + 138 + 160 + 163	40:53:00	167L	43:57:00	0.930	14	0.928	0.933
233'456 - HxCB	160	41411-62-5	129 + 138 + 160 + 163							

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'44'6 - HxCB	158	74472-42-7		41:13:00	167L	43:57:00	0.938	6	0.937	0.939
2344'56 - HxCB	166	41411-63-6	128 + 166							
22'33'44' - HxCB	128	38380-07-3	128 + 166	42:08:00	167L	43:57:00	0.959	10	0.957	0.961
233'455' - HxCB	159	39635-35-3		43:10:00	167L	43:57:00	0.982	6	0.981	0.983
233'4'55' - HxCB	162	39635-34-2		43:28:00	167L	43:57:00	0.989	6	0.988	0.990
23'44'55' - HxCB	167	52663-72-6		43:59:00	167L	43:57:00	1.001	-1,3	1.000	1.001
233'44'5 - HxCB	156	38380-08-4		45:11:00	156L/157L	45:10:00	1.000	6	0.999	1.001
233'44'5' - HxCB	157	69782-90-7	156 + 157							
33'44'55' - HxCB	169	32774-16-6		48:36:00	169L	48:34:00	1.001	-1,3	1.000	1.001
22'34'566' - HpCB	188	74487-85-7		38:06:00	188L	38:04:00	1.001	-1,3	1.000	1.001
22'33'566' - HpCB	179	52663-64-6		38:26:00	188L	38:04:00	1.010	6	1.008	1.011
22'344'66' - HpCB	184	74472-48-3		39:00:00	188L	38:04:00	1.025	6	1.023	1.026
22'33'466' - HpCB	176	52663-65-7		39:22:00	188L	38:04:00	1.034	6	1.033	1.035
22'34566' - HpCB	186	74472-49-4		39:50:00	188L	38:04:00	1.046	6	1.045	1.048
22'33'55'6 - HpCB	178	52663-67-9		41:17:00	188L	38:04:00	1.085	6	1.083	1.086
22'33'45'6 - HpCB	175	40186-70-7		41:57:00	188L	38:04:00	1.102	6	1.101	1.103
22'34'55'6 - HpCB	187	52663-68-0		42:15:00	188L	38:04:00	1.110	6	1.109	1.111
22'344'56' - HpCB	182	60145-23-5		42:27:00	188L	38:04:00	1.115	6	1.114	1.116
22'344'5'6 - HpCB	183	52663-69-1	183 + 185	42:56:00	188L	38:04:00	1.128	6	1.127	1.129
22'3455'6 - HpCB	185	52712-05-7	183 + 185							
22'33'456' - HpCB	174	38411-25-5		43:07:00	188L	38:04:00	1.133	6	1.131	1.134
22'33'4'56 - HpCB	177	52663-70-4		43:35:00	188L	38:04:00	1.145	6	1.144	1.146
22'344'56 - HpCB	181	74472-47-2		44:00:00	188L	38:04:00	1.156	6	1.155	1.157
22'33'44'6 - HpCB	171	52663-71-5	171 + 173	44:13:00	188L	38:04:00	1.162	10	1.159	1.164
22'33'456 - HpCB	173	68194-16-1	171 + 173							
22'33'455' - HpCB	172	52663-74-8		45:57:00	189L	51:13:00	0.897	6	0.896	0.898
233'455'6 - HpCB	192	74472-51-8		46:15:00	189L	51:13:00	0.903	6	0.902	0.904
233'4'55'6 - HpCB	193	69782-91-8	180 + 193							
22'344'55' - HpCB	180	35065-29-3	180 + 193	46:36:00	180L	46:35:00	1.000	6	0.999	1.001
233'44'5'6 - HpCB	191	74472-50-7		47:00:00	189L	51:13:00	0.918	6	0.917	0.919
22'33'44'5 - HpCB	170	35065-30-6		47:57:00	170L	47:56:00	1.000	6	0.999	1.001

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'44'56 - HpCB	190	41411-64-7		48:31:00	189L	51:13:00	0.947	6	0.946	0.948
233'44'55' - HpCB	189	39635-31-9		51:14:00	189L	51:13:00	1.000	-1,3	1.000	1.001
22'33'55'66' - OcCB	202	2136-99-4		43:43:00	202L	43:41:00	1.001	-1,3	1.000	1.001
22'33'45'66' - OcCB	201	40186-71-8		44:41:00	202L	43:41:00	1.023	10	1.021	1.025
22'344'566' - OcCB	204	74472-52-9		45:23:00	202L	43:41:00	1.039	6	1.038	1.040
22'33'44'66' - OcCB	197	33091-17-7	197 + 200	45:41:00	202L	43:41:00	1.046	6	1.045	1.047
22'33'4566' - OcCB	200	52663-73-7	197 + 200							
22'33'455'6 - OcCB	198	68194-17-2	198 + 199	48:40:00	202L	43:41:00	1.114	10	1.112	1.116
22'33'455'6' - OcCB	199	52663-75-9	198 + 199							
22'33'44'56' - OcCB	196	42740-50-1		49:23:00	205L	53:54:00	0.916	6	0.915	0.917
22'344'55'6 - OcCB	203	52663-76-0		49:35:00	205L	53:54:00	0.920	6	0.919	0.921
22'33'44'56 - OcCB	195	52663-78-2		50:59:00	205L	53:54:00	0.946	6	0.945	0.947
22'33'44'55' - OcCB	194	35694-08-7		53:26:00	205L	53:54:00	0.991	6	0.990	0.992
233'44'55'6 - OcCB	205	74472-53-0		53:56:00	205L	53:54:00	1.001	-1,3	1.000	1.001
22'33'455'66' - NoCB	208	52663-77-1		50:43:00	208L	50:42:00	1.000	-1,3	1.000	1.001
22'33'44'566' - NoCB	207	52663-79-3		51:42:00	208L	50:42:00	1.020	6	1.019	1.021
22'33'44'55'6 - NoCB	206	40186-72-9		55:45:00	206L	55:44:00	1.000	-1,3	1.000	1.001
22'33'44'55'66' - DeCB	209	2051-24-3		57:26:00	209L	57:25:00	1.000	-1,3	1.000	1.001
LABELLED COMPOUND										
13C12-2 - MoCB	**1L**			11:34:00	9L	16:05:00	0.719	30	0.704	0.735
13C12-4 - MoCB	**3L**			13:48:00	9L	16:05:00	0.858	30	0.842	0.874
13C12-22' - DiCB	**4L**			14:03:00	9L	16:05:00	0.874	30	0.858	0.889
13C12-44' - DiCB	**15L**			20:08:00	9L	16:05:00	1.252	30	1.236	1.267
13C12-22'6 - TriCB	**19L**			17:13:00	9L	16:05:00	1.070	30	1.055	1.086
13C12-344' - TriCB	**37L**			27:27:00	52L	25:09:00	1.091	30	1.082	1.101
13C12-22'66' - TeCB	**54L**			20:25:00	52L	25:09:00	0.812	20	0.805	0.818
13C12-33'44' - TeCB	**77L**			35:07:00	52L	25:09:00	1.396	20	1.390	1.403
13C12-344'5 - TeCB	**81L**			34:31:00	52L	25:09:00	1.372	20	1.366	1.379
13C12-22'466' - PeCB	**104L**			26:08:00	101L	32:19:00	0.809	20	0.804	0.814
13C12-233'44' - PeCB	**105L**			38:46:00	101L	32:19:00	1.200	20	1.194	1.205
13C12-2344'5 - PeCB	**114L**			38:06:00	101L	32:19:00	1.179	20	1.174	1.184
13C12-23'44'5 - PeCB	**118L**			37:32:00	101L	32:19:00	1.161	20	1.156	1.167
13C12-2'344'5 - PeCB	**123L**			37:12:00	101L	32:19:00	1.151	20	1.146	1.156

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
13C12-33'44'5 - PeCB	126L			42:01:00	101L	32:19:00	1.300	20	1.295	1.305
13C12-22'44'66' - HxCB	155L			32:05:00	138L	40:48:00	0.786	20	0.782	0.790
13C12-233'44'5 - HxCB and	156L			45:10:00	138L	40:48:00	1.107	20	1.103	1.111
13C12-233'44'5' - HxCB	157L									
13C12-23'44'55' - HxCB	167L			43:57:00	138L	40:48:00	1.077	20	1.073	1.081
13C12-33'44'55' - HxCB	169L			48:34:00	138L	40:48:00	1.190	20	1.186	1.194
13C12-22'34'566' - HpCB	188L			38:04:00	194L	53:25:00	0.713	20	0.710	0.716
13C12-233'44'55' - HpCB	189L			51:13:00	194L	53:25:00	0.959	20	0.956	0.962
13C12-22'33'55'66' - OcCB	202L			43:41:00	194L	53:25:00	0.818	20	0.815	0.821
13C12-233'44'55'6 - OcCB	205L			53:54:00	194L	53:25:00	1.009	30	1.004	1.014
13C12-22'33'44'55'6 - NoCB	206L			55:44:00	194L	53:25:00	1.043	30	1.039	1.048
13C12-22'33'455'66' - NoCB	208L			50:42:00	194L	53:25:00	0.949	20	0.946	0.952
13C12-22'344'55' - HpCB	180L			46:35:00	194L	53:25:00	0.872	20	0.869	0.875
13C12-22'33'44'5 - HpCB	170L			47:56:00	194L	53:25:00	0.897	20	0.894	0.900
13C12-22'33'44'55'66' - DeCB	209L			57:26:00	194L	53:25:00	1.075	30	1.071	1.080
LABELLED CLEAN-UP STANDARD										
13C12-244' - TriCB	28L			23:16:00	52L	25:09:00	0.925	20	0.918	0.932
13C12-233'55' - PeCB	111L			35:09:00	101L	32:19:00	1.088	20	1.083	1.093
13C12-22'33'55'6 - HpCB	178L			41:16:00	138L	40:48:00	1.011	20	1.007	1.016
LABELLED INJECTION INTERNAL STANDARD										
13C12-25 - DiCB	9L			16:05:00	138L	40:48:00	0.394	25	0.389	0.399
13C12-22'55' - TeCB	52L			25:09:00	138L	40:48:00	0.616	25	0.611	0.622
13C12-22'455' - PeCB	101L			32:19:00	138L	40:48:00	0.792	25	0.787	0.797
13C12-22'344'5' - HxCB	138L			40:48:00	138L	40:48:00	1.000	100	0.980	1.020
13C12-22'33'44'55' - OcCB	194L			53:25:00	138L	40:48:00	1.309	25	1.304	1.314

(1) Suffix "L" indicates labelled compound.

(2) C = co-eluting congener

Table 6b. Modifications to PCB Nomenclature for EPA CBC01.2 Applications **

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'45' - PeCB	109	70362-41-3	86 + 87 + 97 + 109 + 119 + 125	33:29:00	123L	37:12:00	0.900	16	0.897	0.904
233'4'5 - PeCB	108	70424-68-9	108 + 124	36:50:00	123L	37:12:00	0.990	10	0.988	0.992
233'46 - PeCB	107	74472-35-8		37:05:00	123L	37:12:00	0.997	6	0.996	0.998

** Congeners named PCB 108, 107 and 109 in Method 1668A are named PCB 109, 108 and 107 respectively for EPA CBC01.2 applications

CALIBRATION

Initial calibration is performed using a five point calibration series of solutions that encompass the working concentration range. Initial calibration solutions contain the suite of labelled surrogate and recovery standards and natives listed in the table below. Calibration procedures use the mean RRFs determined from the initial calibration to calculate analyte concentrations. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution. The mid level calibration solution contains 209 PCB congeners and is used to establish the relative response factors and retention times for those PCB congeners not present in the multi-level standards solutions.

Alternately clients may request initial calibration be performed using a six point calibration series of solutions if lower detection limits are required (CS 0.2).

Nominal Concentration of PCB Calibration Solutions

		Concentration (ng/mL)						
	Congener No.[1]	CS-0.2	CS-1	CS-2	CS-3	CS-4	CS-5	Native Standard Amount added to sample
Native Compounds								
2-MoCB	1	0.2	1.0	5.0	50	400	2000	1000 pg
4-MoCB	3	0.2	1.0	5.0	50	400	2000	1000 pg
2,2'-DiCB	4	0.2	1.0	5.0	50	400	2000	1000 pg
4,4'-DiCB	15	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',6-TriCB	19	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,5-TriCB	23	0.2	1.0	5.0	50	400	2000	1000 pg
2',3,5-TriCB	34	0.2	1.0	5.0	50	400	2000	1000 pg

3,4,4'-TriCB	37	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',6,6'-TeCB	54	0.2	1.0	5.0	50	400	2000	1000 pg
3,3',4,4'-TeCB	77	0.2	1.0	5.0	50	400	2000	1000 pg
3,4,4',5-TeCB	81	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',4,6,6'-PeCB	104	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4'-PeCB	105	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,4,4',5-PeCB	114	0.2	1.0	5.0	50	400	2000	1000 pg
2,3',4,4',5-PeCB	118	0.2	1.0	5.0	50	400	2000	1000 pg
2',3,4,4',5-PeCB	123	0.2	1.0	5.0	50	400	2000	1000 pg
3,3',4,4',5-PeCB	126	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',4,4',6,6'-HxCB	155	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5-HxCB	156	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5'-HxCB	157	0.2	1.0	5.0	50	400	2000	1000 pg
2,3',4,4',5,5'-HxCB	167	0.2	1.0	5.0	50	400	2000	1000 pg
3,3',4,4',5,5'-HxCB	169	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3'4,4',5-HpCB	170	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4,4',5,5'-HpCB	180	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4,4',5,6'-HpCB	182	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4',5,5',6-HpCB	187	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4',5,6,6'-HpCB	188	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5,5'-HpCB	189	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',5,5',6,6'-OcCB	202	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5,5',6-OcCB	205	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,4',5,5',6-NoCB	206	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,5,5',6,6'-NoCB	208	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,4',5,5',6,6'-DeCB	209	0.2	1.0	5.0	50	400	2000	1000 pg
Surrogate Standards								**Surrogate Standard Amount added to sample**
$^{13}C_{12}$-2-MoCB	1L[2]	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-3,4,4'-TriCB	37L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100	2000 pg

$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	100	100	100	100	100	2000 pg
Cleanup Standards								
$^{13}C_{12}$-2,4,4'-TriCB	28L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100	100	2000 pg
Recovery Standards								
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100	2000 pg

1. Suffix "L" indicates labelled compound.

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak responses must be at least 2.5 times the background noise level.
2. All peaks are acquired in the appropriate acquisition windows, when compared to the window standard.

3. Peak centroids for the quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 15% of the expected ratio.

Aroclor equivalent concentrations may be calculated by converting the summed concentrations of a suite of characteristic PCB congeners to concentrations using empirical factors determined from the analysis of Aroclor mixtures.

Aroclor 1016[1] = the sum of PCBs 8, 18/30, 31, 28/20 concentrations multiplied by 2.7;
Aroclor 1221 = the sum of PCBs 1, 3, 8 concentrations multiplied by 1.4;
Aroclor 1232 = the sum of PCBs 1, 3, 18/30 concentrations multiplied by 3.4;
Aroclor 1242[1] = the sum of PCBs 8, 18/30, 31, 28/20 concentrations multiplied by 3.0;
Aroclor 1248 = the sum of PCBs 44/47/65, 49/69, 66 concentrations multiplied by 6.1;
Aroclor 1254 = the sum of PCBs 86/87/97/108/119/125, 99 concentrations multiplied by 8.0;
Aroclor 1260 = the sum of PCBs 183/185, 180/193, 170 concentrations multiplied by 5.0;

Environmental samples with no clearly identified Aroclor signature are quantified as 1242/1254/1260 mixtures. Results may be reported as Aroclor 1248 instead of Aroclor 1242 and 1254 where the congener pattern clearly indicates this formulation. Other Aroclor formulations may be reported by calibration against the specific Aroclor solutions.

[1] Aroclors 1016 and 1242 may be reported as combined 1016/1242 using the 1242 factor

REPORTING LIMITS

Concentrations and detection limits for the 209 PCB congeners are reported. Typical reporting units for all data are pg/g, pg/L, or pg/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood and milk) are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous are reported on a volume basis. Concentrations in XAD-2 resin, filters and stack gas samples are reported on a per sample basis or a per volume basis. Concentrations in particulate filters are reported on a per sample basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 2.5 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term(s): Estimated Detection Limit (EDL) from EPA method 8290.

Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-5 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. ((lowest level cal conc.) x (extract volume))/sample size. Typical extract volume for PCBs is 20 µL.

For the analysis of PCBs AXYS standard is to report sample concentrations using the SDL with a minimum reporting limit of 0.5 pg absolute.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.
- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract. For some matrices (XAD columns, filters, air samples) only field duplicates (if available) can be analyzed.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

QC Specification Table: Native and Surrogate Standard Recoveries, CAL/VER, IPR, OPR, and Samples[1]

Congener	Cong. No.[2]	Test conc ng/mL	CAL/VER (%)		IPR (%)		OPR (%)		Labelled compound recovery in samples	
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
2-MoCB	1	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4-MoCB	3	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'-DiCB	4	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4,4'-DiCB	15	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'6-TrCB	19	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4'-TrCB	37	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'6,6'TeCB	54	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4'-TeCB	77	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4',5-TeCB	81	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,6,6'-PeCB	104	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4'-PeCB	105	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,4,4',5-PeCB	114	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5-PeCB	118	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2',3,4,4',5-PeCB	123	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5-PeCB	126	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,4',6,6'-HxCB	155	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5-HxCB[3]	156	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5'-HxCB[3]	157	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5,5'-HxCB	167	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5,5'-HxCB	169	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,4',5,6,6'-HpCB	188	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5'-HpCB	189	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',5,5',6,6'-OcCB	202	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5',6-OcCB	205	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',4,4',5,5',6-NoCB	206	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3,'4,5,5',6,6'-NoCB	208	50	75-125	70-130	40	60-140	70-130	50-150	-	-
DeCB	209	50	75-125	70-130	40	60-140	70-130	50-150	-	-
Labelled Compounds										
$^{13}C_{12}$-2-MoCB	1L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
$^{13}C_{12}$-4-MoCB	3L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
$^{13}C_{12}$-2,2'-DiCB	4L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
$^{13}C_{12}$-4,4'-DiCB	15L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
$^{13}C_{12}$-2,2',6-TrCB	19L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,3',4,4'-TCB	77L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150

Congener	Cong. No.[2]	Test conc ng/mL	CAL/VER (%)		IPR (%)		OPR (%)		Labelled compound recovery in samples	
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5-HxCB[3]	156L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[3]	157L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB	189L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
Cleanup Standard										
$^{13}C_{12}$-2,4,4'-TriCB	28L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
2. Suffix "L" indicates labelled compound.
3. PCBs 156 and 157 are tested as the sum of two concentrations

QC Specification Table: QC Samples, Instrumental Analysis, and Analyte Quantification

QC Parameter	Specification
Analysis Duplicate Guideline	Agree to within ±20% of the mean (applicable to concentrations >10 times the DL)[1]
Procedural Blank	Analyte concentrations in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be less than 2 pg/congener/sample, and concentrations of PCB congeners 156, 157, 167 and 189 must be less than 10 pg/congener/sample. Concentrations of all other individual PCB congeners or coelutions must be less than 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be less than 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times the blank levels.
Sample Specific Detection Limit	Typical sample specific detection limits, determined from chromatographic noise, are in the range of 0.5 to 2.0 pg.
Initial Calibration	For 6-point calibration, a relative standard deviation of the RRF's ≤20% for all compounds Ion ratios for all congeners must be within ±15% of theoretical for CS 0.2. Minimum S:N ratio 10:1 for all calibration standards. For CS0.2, S:N ratio may be as low as 3:1 for di-PCBs and nona-PCBs.
Continuing CAL VER	Refer to Table 4 above.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Ion ratios must fall within ±15% of the theoretical values for positive identification of all targets in the calibration standards and samples.
Sensitivity	Minimum S:N ratio 10:1 for all calibration standards. For CS0.2, S:N ratio may be as low as 3:1. for di-PCBs and nona-PCBs.

[1.] Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

REFERENCES:

1. EPA Method 1668, Revision A - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, with changes and corrections through to August 20, 2003.*

2. EPA Method CBC01.2 *Statement of Work (SOW) for Analysis of Chlorinated Biphenyl Congeners (CBCS),* December 2009.

APPENDIX A

SUMMARY OF MODIFICATIONS TO EPA METHOD 1668A

The following sections of EPA Method 1668A have been modified as described below.

Section 4.2.1, 4.2.2: The protocol for washing reusable glassware includes a detergent wash, water rinse and baking at a minimum of 300°C for 8 hours. Immediately prior to use, glassware is solvent rinsed with toluene and hexane.

Section 4.7: The first cleanup column for tissue extracts is a gravity gel permeation column (SX-3 Biobeads). An anthropogenic isolation column 7.5.3 is not used.

Section 6.5.1: Glass wool is cleaned by rinsing twice with toluene and twice with hexane.

Section 7.12, 7.13, 9.0, 11.0: The concentration of the labelled toxics/LOC and the cleanup standard spiking solutions is 100 ng/mL and the sample spiking volume is 20 µL. The resulting final concentrations in the extracts are as specified in the method.

Section 7.14: Concentration of the labelled injection internal standard spiking solution (recovery standard) is modified so that a volume of 5 µL is added. The resulting amount of standard added to the final extract is the same as specified in the method. The solution is spiked into a 15 µL extract volume for a final extract volume of 20 µL.

Section 7.2.1: Sodium sulphate is baked at a minimum of 300°C for 8 hrs rather than at 600°C for 24 hrs.

Section 7.5.1: Silica is activated by baking at 450°C in a muffle oven for at least 8 hrs.

Section 7.5.4.1.1: Florisil is baked at 450°C in a muffle over for at least 8 hrs, then deactivated with water to 2.1% deactivation.

Section 10.3.3, 15.3.3: A S:N ratio of 3:1 for di-PCBs and nona-PCBs in CS0.2 calibration solution is acceptable.

Section 11.5.6: Unless requested by the client, the aqueous portion after filtration of aqueous samples with >1% solids is not discarded but is extracted.

Section 11.5, 11.5.2, 11.5.5, 12.3 Solid samples are dried by mixing with anhydrous sodium sulphate. The dried solid is extracted using a soxhlet extraction apparatus. The surrogate spike is incorporated after the drying step. Equilibration time for the surrogate is 30 minutes. The extracting solvent for solids is dichloromethane.

Section 12.4, 11.8: The surrogate spike is incorporated into the sample after the drying step to eliminate the possibility of disproportional loss of volatile labelled and target compounds.

Section 12.4.2: The precleaning of the soxhlet apparatus is carried out using toluene instead of dichloromethane, for 2 hours.

Section 12.4.9: Lipid analysis is carried out by sub-sampling two 2 g portions of the extract from a total 30 g extract weight. The cleanup standard is spiked into the extract after soxhlet extraction and before any lipid analysis or rotary evaporation is done. The percent surrogate recoveries are corrected for the amount of extract used for lipid analysis.

Section 12.6.1.1: Rotary evaporation is done at 30°C. Daily cleaning of the rotary evaporators include dismantling and rinsing/soaking with solvent. Mimic proofs are run periodically but are not archived daily.

Section 12.7.4: Before Florisil or alumina cleanup procedures, a solvent exchange is done by reducing under nitrogen to 300 uL and bulking up to 1mL in hexane. If toluene is present the extract is reduced to 50 uL under nitrogen and bulked up to 1mL.

Section 12.7.7: Toluene (1 mL) is added to the eluate from the final column prior to rotary evaporation and nitrogen blow down concentration steps.

Section 13.1.1: GPC chromatography, by a gravity column, is routinely used only for tissue extracts. The GPC cleanup is optional for all other matrices.

Section 13.3.1: Routine layered silica column is as follows: 0.5 g neutral silica, 2 g 28% basic silica, 0.5 g neutral silica, 4 g 44% acidic silica, 4 g 22% acidic silica, 1 g neutral silica.

Section 13.3.4: The sample is loaded onto the column followed by 2-3 rinses of a least 1 mL, and eluted with 100mL of hexane.

Section 14.2: The volume of labelled injection internal standard (recovery standard) added to the extract is 5 µL, for a final extract volume of 20 µL. Hexane rather than nonane is used as the solvent to bring extract back to volume for re-analysis or to dilute extracts.

Section 15.3: The calibration solution containing all 209 PCB congeners is used as the CAL/VER solution.

Section 17.5: Extracts are diluted with hexane. The concentration of the labelled injection internal (recovery) standard is not re-adjusted to 100 pg/uL when dilutions are performed.

Section 17.0

$Conc_i$ - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound *i*)
A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify *i*)
M_x = mass of sample taken for analysis
M_{si} = mass of labelled surrogate (compound *si*) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)
$RRF_{i,si}$ = mean relative response factor of *i* to *si* from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:

Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%\mathrm{Recovery} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;
M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;
$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

Appendix G

Axys Analytical PBDE Analysis SOP

METHOD SUMMARY

ANALYTICAL METHOD FOR THE DETERMINATION OF BROMINATED DIPHENYL ETHERS (BDE) BY EPA METHOD 1614

This method describes the determination of the concentrations of a selected suite of brominated diphenylethers (BDE) in a variety of environmental samples, according to the protocols described in EPA Method 1614 and conducted by AXYS Method MLA-033. It further describes semi-quantitative analysis of four non-BDE brominated flame retardants (BFR) in POTW biosolids and effluents. Samples are spiked with 13C-labelled surrogate standards prior to analysis. Samples are extracted; the extracts cleaned up by column chromatography and analyzed by high-resolution gas chromatography with high-resolution mass spectrometric detection (HRGC-HRMS).

Typical reporting limits for BDEs range from 1 – 2 pg/sample for the DiBDE through HpBDE and 10 – 20 pg/sample for NoBDE and DeBDE.

BDE Target Analytes

BDE Congener	BDE No.	BDE Congener	BDE No.
2,4-DiBDE	7	2,2',3,4,4'-PeBDE	85
2,4'-DiBDE	8	**2,2',4,4',5-PeBDE***	**99**
2,6-DiBDE	10	**2,2',4,4',6-PeBDE***	**100**
3,3'-DiBDE	11	2,3,3',4,4'-PeBDE	105
3,4-DiBDE	12	2,3,4,5,6-PeBDE	116
3,4'-DiBDE	13	2,3',4,4',6-PeBDE	119
4,4'-DiBDE	15	2,3',4,5,5'-PeBDE	120
2,2',4-TrBDE	17	3,3',4,4',5-PeBDE	126
2,3',4-TrBDE	25	2,2',3,3',4,4'-HxBDE	128
2,4,4'-TrBDE*	**28**	2,2',3,4,4',5'-HxBDE	138
2,4,6-TrBDE	30	2,2',3,4,4',6'-HxBDE	140
2,4',6-TrBDE	32	**2,2',4,4',5,5'-HxBDE***	**153**
2',3,4-TrBDE	33	**2,2',4,4',5,6'-HxBDE***	**154**
3,3',4-TrBDE	35	2,2',4,4',6,6'-HxBDE	155
3,4,4'-TrBDE	37	2,3,4,4',5,6-HxBDE	166
2,2',4,4'-TeBDE*	**47**	2,2',3,4,4',5,6-HpBDE	181
2,2',4,5'-TeBDE	49	**2,2',3,4,4',5',6-HpBDE***	**183**
2,2',4,6'-TeBDE	51	2,3,3',4,4',5,6-HpBDE	190
2,3',4,4'-TeBDE	66	2,2',3,4,4',5,5',6-OcBDE	203
2,3',4',6-TeBDE	71	2,2',3,3',4,4',5,5',6-NoBDE	206 **
2,4,4',6-TeBDE	75	2,2',3,3',4,4',5,6,6'-NoBDE	207 **
3,3',4,4'-TeBDE	77	2,2',3,3',4,5,5',6,6'-NoBDE	208 **
3,3',4,5'-TeBDE	79	**2,2',3,3',4,4',5,5',6,6'-DeBDE***	**209**

* BDE congeners of "Primary Interest" as defined by EPA Method 1614.

** BDEs 206, 207 and 208 may be formed from BDE 209 degradation during the analysis procedure and results reported for these congeners represent maximum concentrations.

Non-BDE BFR Target Compound Suite

Abbreviation	**Full Name** (Wellington Labs Supplier)	**CA Index Name**	**CAS No.**
HBB	Hexabromobenzene	1,2,3,4,5,6-hexabromobenzene	87-82-1
PBEB	Pentabromoethylbenzene	1,2,3,4,5-pentabromo-6-ethylbenzene	85-22-3
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane	1,1'-(1,2-ethanediylbis(oxy))bis(2,4,6-tribromobenzene)	37853-59-1
DBDPE	Decabromodiphenylethane	1,1'-(1,2- ethanediyl)bis(2,3,4,5,6-pentabromobenzene)	84852-53-9

1.0 EXTRACTION AND CLEANUP PROCEDURES

Samples are spiked with isotopically labelled BDE surrogate standards, solvent extracted, spiked with a cleanup surrogate standard and cleaned up on a series of chromatographic columns which may include layered acid/base silica, Florisil and alumina columns. The final extract is spiked with isotopically labelled recovery (internal) standards prior to instrumental analysis.

2.0 INSTRUMENTATION

Analysis of BDE is performed using a capillary gas chromatograph coupled to an HRMS. A DB-5HT capillary column (30 m, 0.25 mm i.d. x 0.1 µm film thickness) is coupled to the MS source. Immediately prior to running samples the mass spectrometer is tuned to have a static mass resolution of 5,000. The instrument is mass calibrated against PFK reference and profiles of fragment ions are printed to demonstrate dynamic mass resolution. Data are acquired in voltage selected ion recording mode (V-SIR) using selected PFK ions as a reference for mass lock. Two masses from the molecular ion cluster are used to monitor each of the target analytes and 13C12-labelled surrogate standards.

3.0 CALIBRATION

A series of calibration solutions covering the working response range of the instrument (CS-1 through CS-5) containing BDEs of Primary Interest and labelled surrogate, cleanup and recovery standards is used to establish initial, multi-level calibration of the GC/MS. An additional, single point calibration solution containing all target BDE analytes is used to determine the relative response factors and retention times of the BDE congeners that are not present in the initial calibration solutions. The single point solution is also used as the calibration verification (CAL-VER) solution, which is analyzed every 12 hours, to demonstrate stability of calibration.

The sample equivalent lower method calibration limit (LMCL) is defined as the concentration of the lowest calibration solution pro-rated for sample size analyzed and final extract volume.

Table: 1 Nominal Concentration of BDE Calibration Solutions HRGC/HRMS Analysis

	Nominal Concentration (ng/mL)				
Authentic Analyte	**CS-1**	**CS-2**	**CS-3**	**CS-4**	**CS-5**
BDE 28	1	5	50	500	2500
BDE 47	1	5	50	500	2500
BDE 99	1	5	50	500	2500
BDE 100	1	5	50	500	2500
BDE 153	1	5	50	500	2500
BDE 154	1	5	50	500	2500
BDE 183	1	5	50	500	2500
BDE 209	10	50	500	5000	25000
Labelled Cleanup Std					
$^{13}C_{12}$-BDE 139	100	100	100	100	100
Labelled Surrogate Stds					
$^{13}C_{12}$-BDE 15	100	100	100	100	100
$^{13}C_{12}$-BDE 28	100	100	100	100	100
$^{13}C_{12}$-BDE 47	100	100	100	100	100
$^{13}C_{12}$-BDE 77	100	100	100	100	100
$^{13}C_{12}$-BDE 99	100	100	100	100	100
$^{13}C_{12}$-BDE 100	100	100	100	100	100
$^{13}C_{12}$-BDE 126	100	100	100	100	100
$^{13}C_{12}$-BDE 153	100	100	100	100	100
$^{13}C_{12}$-BDE 154	100	100	100	100	100
$^{13}C_{12}$-BDE 183	100	100	100	100	100
$^{13}C_{12}$-BDE 197	100	100	100	100	100
$^{13}C_{12}$-BDE 209	1000	1000	1000	1000	1000
Labelled Recovery Stds					
$^{13}C_{12}$-BDE 79	100	100	100	100	100
$^{13}C_{12}$-BDE 180	100	100	100	100	100
$^{13}C_{12}$-BDE 206	400	400	400	400	400

4.0 QUANTIFICATION PROCEDURES

Calculations

$Conc_i$ - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound *i*)

A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify *i*)

M_x = mass of sample taken for analysis

M_{si} = mass of labelled surrogate (compound *si*) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)

$RRF_{i,si}$ = mean relative response factor of *i* to *si* from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:
Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%\text{Recovery} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;
M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;
$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

.

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

4.1 Reporting Limits

Sample specific detection limits (SDLs) reported with the analytical results are determined from the analysis data by converting the minimum detectable signal to a concentration following the same procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as 2.5 times the height of the noise in the m/z channel of interest, converted to an area using the area height ratio of the corresponding labelled surrogate peak.

Table 2. Polybrominated Diphenylethers (PBDE) by HRGC/HRMS, Surrogates Used, RRF Determination and Ions Monitored

COMPOUND	IUPAC NO.	RT Ref.	Typical RT (m:ss)	Nominal RRT	RRT Limits	RT Window (sec.)	Quantification Reference	Mass1	Mass2	m1/m2 ratio	Ion ratio Limits
2,6-DiBDE	10	15L	15:48	0.8642	0.8459 – 0.8824	± 20	15L	325.8942	327.8921	0.51	0.43 – 0.59
2,4-DiBDE	7	15L	16:59	0.9289	0.9152 - 0.9426	± 15	15L	325.8942	327.8921	0.51	0.43 – 0.59
2,4'-DiBDE/3,3-DiBDE [c]	8/11	15L	17:32	0.9590	0.9499 – 0.9681	± 10	15L	325.8942	327.8921	0.51	0.43 – 0.59
3,4-DiBDE	12	15L	17:50	0.9754	0.9663 – 0.9845	± 10	15L	325.8942	327.8921	0.51	0.43 – 0.59
3,4'-DiBDE	13	15L	17:54	0.9790	0.9699 – 0.9881	± 10	15L	325.8942	327.8921	0.51	0.43 – 0.59
4,4'-DiBDE	15	15L	18:18	1.0009	0.9991 – 1.0036	-2 +3	15L	325.8942	327.8921	0.51	0.43 – 0.59
2,4,6-TrBDE	30	28L	20:26	0.8955	0.8809 – 0.9102	± 20	28L	405.8027	407.8002	1.03	0.88 – 1.18
2,4',6-TrBDE	32	28L	21:45	0.9533	0.9459 – 0.9606	± 10	28L	405.8027	407.8002	1.03	0.88 – 1.18
2,2',4-TrBDE	17	28L	22:11	0.9722	0.9649 – 0.9795	± 10	28L	405.8027	407.8002	1.03	0.88 – 1.18
2,3',4-TrBDE	25	28L	22:17	0.9766	0.9693 – 0.9839	± 10	28L	405.8027	407.8002	1.03	0.88 – 1.18
2,4,4'-TrBDE/2',3,4-TrBDE [c]	28/33	28L	22:49	1.0000	0.9985 – 1.0022	-2 +3	28L	405.8027	407.8002	1.03	0.88 – 1.18
3,3',4-TrBDE	35	28L	23:14	1.0183	1.0110 – 1.0256	± 10	28L	405.8027	407.8002	1.03	0.88 – 1.18
3,4,4'-TrBDE	37	28L	23:41	1.0380	1.0307 – 1.0453	± 10	28L	405.8027	407.8002	1.03	0.88 – 1.18
2,4,4',6'-TeBDE	75	47L	26:04	0.9625	0.9563 – 0.9686	± 10	47L / 77L	483.7132	485.7111	0.70	0.60 – 0.81
2,2',4,6'-TeBDE	51	47L	26:12	0.9674	0.9612 – 0.9735	± 10	47L / 77L	483.7132	485.7111	0.70	0.60 – 0.81
2,2',4,5'-TeBDE	49	47L	26:25	0.9754	0.9692 – 0.9815	± 10	47L / 77L	483.7132	485.7111	0.70	0.60 – 0.81
2,3',4',6-TeBDE	71	47L	26:33	0.9803	0.9742 – 0.9865	± 10	47L / 77L	483.7132	485.7111	0.70	0.60 – 0.81
2,2',4,4'-TeBDE	47	47L	27:05	1.0000	0.9988 – 1.0018	-2 +3	47L	483.7132	485.7111	0.70	0.60 – 0.81
3,3',4,5'-TeBDE	79	47L	27:26	1.0123	1.0062 – 1.0185	± 10	47L / 77L	483.7132	485.7111	0.70	0.60 – 0.81
2,3',4,4'-TeBDE	66	47L	27:40	1.0215	1.0154 – 1.0277	± 10	47L / 77L	483.7132	485.7111	0.70	0.60 – 0.81
3,3',4,4'-TeBDE	77	47L	28:34	1.0000	0.9988 - 1.0018	-2 +3	77L	483.7132	485.7111	0.70	0.60 – 0.81
2,2',4,4',6-PeBDE	100	100L	30:10	1.0000	0.9989 – 1.0017	-2 +3	100L	563.6216	565.6196	1.03	0.88 – 1.18
2,3',4,4',6-PeBDE/2,3',4,5,5'-PeBDE [c]	119/120	100L	30:28	1.0099	1.0044 – 1.0155	± 10	99L/100L/126L	563.6216	565.6196	1.03	0.88 – 1.18
2,2',4,4',5-PeBDE	99	99L	31:04	1.0005	0.9995 – 1.0021	-2 +3	99L	563.6216	565.6196	1.03	0.88 – 1.18
2,3,4,5,6-PeBDE	116	99L	31:19	1.0086	1.0032 – 1.0140	± 10	99L/100L/126L	563.6216	565.6196	1.03	0.88 – 1.18
2,2',3,4,4'-PeBDE	85	126L	32:34	0.9914	0.9863 – 0.9964	± 10	99L/100L/126L	563.6216	565.6196	1.03	0.88 – 1.18
3,3',4,4',5-PeBDE	126	126L	32:51	1.0000	0.9990 – 1.0015	-2 +3	126L	563.6216	565.6196	1.03	0.88 – 1.18
2,3,3',4,4'-PeBDE	105	126L	33:08	1.0086	1.0036 – 1.0137	± 10	99L/100L/126L	563.6216	565.6196	1.03	0.88 – 1.18

COMPOUND	IUPAC NO.	RT Ref.	Typical RT (m:ss)	Nominal RRT	RRT Limits	RT Window (sec.)	Quantification Reference	Mass1	Mass2	m1/m2 ratio	Ion ratio Limits
2,2',4,4',6,6'-HxBDE	155	154L	32:50	0.9816	0.9766 – 0.9865	± 10	153L / 154L	641.5322	643.5302	0.77	0.65 – 0.89
2,2',4,4',5',6-HxBDE	154	154L	33:28	1.0005	0.9995 – 1.0020	-2 +3	154L	641.5322	643.5302	0.77	0.65 – 0.89
2,2',4,4',5,5'-HxBDE	153	153L	34:38	1.0005	0.9995 – 1.0019	-2 +3	153L	641.5322	643.5302	0.77	0.65 – 0.89
2,2',3,4,4',6'-HxBDE	140	153L	35:20	1.0207	1.0159 – 1.0255	± 10	153L / 154L	641.5322	643.5302	0.77	0.65 – 0.89
2,2',3,4,4',5'-HxBDE/ 2,3,4,4',5,6-HxBDE [c]	138/166	153L	36:09	1.0443	1.0395 – 1.0491	± 10	153L / 154L	641.5322	643.5302	0.77	0.65 – 0.89
2,2',3,3',4,4'-HxBDE	128	153L	37:43	1.0896	1.0823 – 1.0968	± 15	153L / 154L	641.5322	643.5302	0.77	0.65 – 0.89
2,2',3,4,4',5',6-HpBDE	183	183L	37:58	1.0000	0.9991 – 1.0013	-2 +3	183L	721.4406	723.4386	1.03	0.88 – 1.18
2,2',3,4,4',5,6-HpBDE	181	183L	39:40	1.0448	1.0404 – 1.0492	± 10	183L	721.4406	723.4386	1.03	0.88 – 1.18
2,3,3',4,4',5,6-HpBDE	190	183L	39:54	1.0509	1.0465 – 1.0553	± 10	183L	721.4406	723.4386	1.03	0.88 – 1.18
2,2',3,4,4',5,6,6'-OcBDE/ 2,2',3,3',4,4',6,6'-OcBDE [c]	204/197	197L	41:44	1.0004	0.9972-1.0016	-8 +3	197L	799.3511	801.3491	0.82	0.70 – 0.94
2,2',3,4,4',5,5',6-OcBDE	203	197L	42:15	1.0128	1.0088-1.0168	± 10	197L	799.3511	801.3491	0.82	0.70 – 0.94
2,3,3',4,4',5,5',6-OcBDE	205	197L	43:07	1.0336	1.0296-1.0376	± 10	197L	799.3511	801.3491	0.82	0.70 – 0.94
2,2',3,3',4,5,5',6,6'-NoBDE	208	197L	45:32	1.0915	1.0855 -1.0975	± 15	197L	879.2596	881.2575	1.03	0.88 – 1.18
2,2',3,3',4,4',5,6,6'-NoBDE	207	197L	45:52	1.0995	1.0935 -1.1055	± 15	197L	879.2596	881.2575	1.03	0.88 – 1.18
2,2',3,3',4,4',5,5',6-NoBDE	206	197L	46:32	1.1155	1.1095 -1.1215	± 15	197L	879.2596	881.2575	1.03	0.88 – 1.18
DeBDE	209	209L	50:20	1.0000	0.9993 – 1.0010	-2 +3	209L	957.1701	959.1680	0.86	0.73 – 0.99
LABELLED COMPOUNDS											
$^{13}C_{12}$-4,4'-DiBDE	15L	79L	18:18	0.6671	0.6549 – 0.6792	± 20	79L	337.9344	339.9324	0.51	0.43 – 0.59
$^{13}C_{12}$-2,4,4'-TrBDE	28L	79L	22:49	0.8317	0.8226 – 0.8408	± 15	79L	417.8429	419.8409	1.03	0.88 – 1.18
$^{13}C_{12}$-2,2',4,4'-TeBDE	47L	79L	27:04	0.9866	0.9806 – 0.9927	± 10	79L	497.7514	499.7493	1.54	1.31 – 1.77
$^{13}C_{12}$-3,3',4,4'-TeBDE	77L	79L	28:33	1.0407	1.0346 – 1.0468	± 10	79L	497.7514	499.7493	1.54	1.31 – 1.77
$^{13}C_{12}$-2,2',4,4',6-PeBDE	100L	79L	30:09	1.0990	1.0899 – 1.1081	± 15	79L	575.6619	577.6598	1.03	0.88 – 1.18
$^{13}C_{12}$-2,2',4,4',5-PeBDE	99L	79L	31:02	1.1312	1.1221 – 1.1403	± 15	79L	575.6619	577.6598	1.03	0.88 – 1.18
$^{13}C_{12}$-3,3',4,4',5-PeBDE	126L	79L	32:50	1.1968	1.1877 – 1.2060	± 15	79L	575.6619	577.6598	1.03	0.88 – 1.18
$^{13}C_{12}$-2,2',4,4',5',6-HxBDE	154L	180L	33:26	0.8514	0.8451 – 0.8578	± 15	180L	655.5704	657.5683	1.37	1.16 – 1.58
$^{13}C_{12}$-2,2',4,4',5,5'-HxBDE	153L	180L	34:37	0.8816	0.8752 – 0.8879	± 15	180L	655.5704	657.5683	1.37	1.16 – 1.58
$^{13}C_{12}$-2,2',3,4,4',5',6-HpBDE	183L	180L	37:56	0.9660	0.9618 – 0.9703	± 10	180L	733.4809	735.4788	1.03	0.88 – 1.18
$^{13}C_{12}$-2,2',3,3',4,4',6,6'-OcBDE	197L	180L	41:43	1.0624	1.0560 – 1.0688	± 15	180L	811.3914	813.3893	0.82	0.70 – 0.94
$^{13}C_{12}$-DeBDE	209L	206L	50:18	1.0813	1.0760 – 1.0867	± 15	206L	971.2083	973.2063	1.23	1.05 – 1.41

LABELLED CLEAN-UP STANDARD	IUPAC NO.	RT Ref.	Typical RT (m:ss)	Nominal RRT	RRT Limits	RT Window (sec.)	Quantification Reference	Mass1	Mass2	m1/m2 ratio	Ion ratio Limits
$^{13}C_{12}$-2,2',3,4,4',6-HxBDE	139L	153L	35:02	1.0120	1.0072 – 1.0169	± 10	180L	655.5704	657.5683	1.37	1.16 – 1.58
LABELLED FIELD STANDARD											
$^{13}C_{12}$-2,2',3,4,4',5'-HxBDE	138L	153L	36:09	1.0443	1.0395 – 1.0491	± 10	154L	655.5704	657.5683	1.37	1.16 – 1.58
LABELLED INJECTION (RECOVERY) STANDARD											
$^{13}C_{12}$ – 3,3',4,5' - TeBDE	79L	180L	27:26	0.6986	0.6859 – 0.7114	± 30	180L	497.7514	499.7493	1.54	1.31 – 1.77
$^{13}C_{12}$ - 2,2',3,4,4',5,5' – HpBDE	180L	180L	39:16	1.0000	1.0000 – 1.0000	± 100	180L	733.4809	735.4788	1.03	0.88 – 1.18
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoBDE	206L	180L	46:31	1.1846	1.1719 – 1.1974	± 30	180L	891.2998	893.2978	1.03	0.88 – 1.18

(1) Suffix "L" indicates labelled compound.

(2) C = co-eluting congener

5.0 QUALITY ACCEPTANCE CRITERIA

Samples are analyzed in batches consisting of a maximum of twenty samples, one procedural blank and one spiked matrix (OPR) sample. A duplicate is analyzed, provided there is sufficient sample, with batches containing 7-20 samples. Matrix spike/matrix spike duplicate (MS/MSD) pairs may be analyzed on an individual contract basis. The batch is carried through the complete analytical process as a unit. For sample data to be reportable, the batch QC data must meet the established acceptance criteria presented on the analysis reports.

Table 3:QC Acceptance Criteria for Calibration, OPR and Sample Recovery

Compound Name	BDE No.	Initial Calibration	Calibration Verification		OPR Test	Samples		
		% RSD of RRFs	% Actual Concentration		% Actual Concentration	% Recovery		
			Warning Limit for Opening CAL-VER	Acceptance Limit for Opening and Closing CAL-VER		Warning Limit	Acceptance Limit	EPA 1614 Limits
NATIVE COMPOUND								
2,4,4'-TrBDE	28	<20%	-	70-130	50-150	-	-	
2,2',4,4'-TeBDE	47	<20%	-	70-130	50-150	-	-	
2,2',4,4',5-PeBDE	99	<20%	-	70-130	50-150	-	-	
2,2',4,4',6-PeBDE	100	<20%	-	70-130	50-150	-	-	
2,2',4,4',5,5'-HxBDE	153	<20%	-	70-130	50-150	-	-	
2,2',4,4',5,6'-HxBDE	154	<20%	-	70-130	50-150	-	-	
2,2',3,4,4',5',6-HpBDE	183	<20%	-	70-130	50-150	-	-	
2,2',3,3',4,4',5,5',6,6'-DeBDE	209	<20%	-	70-130	50-150	-	-	
SURROGATE STANDARDS								
$^{13}C_{12}$-4,4'-DiBDE	15L	<35%	70-130	50-150	30-200	40-150	25-200	-
$^{13}C_{12}$-2,4,4'-TrBDE	28L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-2,2',4,4'-TeBDE	47L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-3,3',4,4'-TeBDE	77L	<35%	70-130	50-150	30-200	40-150	25-200	
$^{13}C_{12}$-2,2',4,4',5-PeBDE	99L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-2,2',4,4',6-PeBDE	100L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-3,3',4,4',5-PeBDE	126L	<35%	70-130	50-150	30-200	40-150	25-200	
$^{13}C_{12}$-2,2',4,4',5,5'-HxBDE	153L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-2,,2',4,4',5,6'-HxBDE	154L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-2,2',3,4,4',5',6-HpBDE	183L	<35%	70-130	50-150	30-200	40-150	25-200	25-150
$^{13}C_{12}$-2,2',3,3',4,4',6,6'-OcBDE	197L	<35%	70-130	50-150	30-200	40-150	25-200	
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeBDE	209L	<100%	NQ[1]	NQ[1]	10-200	20-200	10-400	20-200
CLEANUP STANDARD								
$^{13}C_{12}$-2,2',3,4,4',6-HxBDE	139L	<35%	70-130	50-150	30-200	40-150	25-200	30-135
FIELD STANDARD								
$^{13}C_{12}$-2,2',3,4,4',5'-HxBDE	138L	<35%	70-130	50-150	50-150	-	50-150	-

[1] NQ = Not Quantified. Refer to Table 5B for in-house GC/MS specification for BDE 209L.

Table 4: BDE Detection Limits and Procedural Blank Criteria

ANALYTE	BDE Number	Typical Sample Specific Detection Limits				Procedural Blank Warning Limit pg/sample	Procedural Blank Acceptance Limit pg/sample
		Solid pg/g	Tissue pg/g	Aqueous pg/L	Air pg/sample		
2,4-DiBDE	7	1	1	10	10	10	20
2,4'-DiBDE	8	1	1	10	10	10	20
2,6-DiBDE	10	1	1	10	10	10	20
3,3'-DiBDE	11	1	1	10	10	10	20
3,4-DiBDE	12	1	1	10	10	10	20
3,4'-DiBDE	13	1	1	10	10	10	20
4,4'-DiBDE	15	1	1	10	10	10	20
2,2',4-TrBDE	17	1	1	10	10	10	20
2,3',4-TrBDE	25	1	1	10	10	10	20
2,4,4'-TrBDE	28	1	1	10	10	10	20
2,4,6-TrBDE	30	1	1	10	10	10	20
2,4',6-TrBDE	32	1	1	10	10	10	20
2',3,4-TrBDE	33	1	1	10	10	10	20
3,3',4-TrBDE	35	1	1	10	10	10	20
3,4,4'-TrBDE	37	1	1	10	10	10	20
2,2',4,4'-TeBDE	47	1	1	10	10	100	150
2,2',4,5'-TeBDE	49	1	1	10	10	10	20
2,2',4,6'-TeBDE	51	1	1	10	10	10	20
2,3',4,4'-TeBDE	66	1	1	10	10	10	20
2,3',4',6-TeBDE	71	1	1	10	10	10	20
2,4,4',6-TeBDE	75	1	1	10	10	10	20
3,3',4,4'-TeBDE	77	1	1	10	10	10	20
3,3',4,5'-TeBDE	79	1	1	10	10	10	20
2,2',3,4,4'-PeBDE	85	1	1	10	10	10	20
2,2',4,4',5-PeBDE	99	1	1	10	10	100	150
2,2',4,4',6-PeBDE	100	1	1	10	10	20	50
2,3,3',4,4'-PeBDE	105	1	1	10	10	10	20
2,3,4,5,6-PeBDE	116	1	1	10	10	10	20
2,3',4,4',6-PeBDE	119	1	1	10	10	10	20
2,3',4,5,5'-PeBDE	120	1	1	10	10	10	20
3,3',4,4',5-PeBDE	126	1	1	10	10	10	20
3,3',4,4',5-PeBDE	128	1	1	10	10	10	20
2,2',3,4,4',5'-HxBDE	138	1	1	10	10	10	20
2,2',3,4,4',6'-HxBDE	140	1	1	10	10	10	20
2,2',4,4',5,5'-HxBDE	153	1	1	10	10	10	20
2,2',4,4',5,6'-HxBDE	154	1	1	10	10	10	20
2,2',4,4',6,6'-HxBDE	155	1	1	10	10	10	20
2,3,4,4',5,6-HxBDE	166	1	1	10	10	10	20

Table 4 Cont'd

ANALYTE	BDE Number	Typical Sample Specific Detection Limits				Procedural Blank Warning Limit pg/sample	Procedural Blank Acceptance Limit pg/sample
		Solid pg/g	Tissue pg/g	Aqueous pg/L	Air pg/sample		
2,2',3,4,4',5,6-HpBDE	181	2	2	20	20	20	30
2,2',3,4,4',5',6-HpBDE	183	2	2	20	20	20	30
2,3,3',4,4',5,6-HpBDE	190	2	2	20	20	20	30
2,2',3,3',4,4',6,6'-OcBDE	197	2	2	20	20	20	30
2,2',3,4,4',5,5',6-OcBDE	203	2	2	20	20	20	30
2,2',3,4,4',5,6,6'-OcBDE	204	2	2	20	20	20	30
2,3,3',4,4',5,5',6-OcBDE	205	2	2	20	20	20	30
2,2',3,3',4,4',5,5',6-NoBDE	206	10	10	100	100	100	200
2,2'3,3',4,4',5,6,6'-NoBDE	207	10	10	100	100	100	200
2,2',3,3',4,5,5',6,6'-NoBDE	208	10	10	100	100	100	200
2,2',3,3',4,4',5,5',6,6'-DeBDE	209	20	20	200	200	2000	3000
Typical Sample Size:		10 g dry	10 g wet	1 L	1 sample		
BDE- Typical Final Vol, µL		50	50 20 for Blood	50	50		
BDE/PCB –Typical Final Vol, µL		20	20	20	20		

Additional QC Criteria

QC Parameter	Specification
Closing CAL VER (internal specification only, applies to all target compound in CAL)	Within ±20% of Opening CAL- VER for all natives compounds except BDE 203, 206, 207, 208 Within ±35% of Opening CAL-VER for BDE 203, 206, 207, 208 Within ±35% of the Opening CAL-VER for ^{13}C-surrogates except ^{13}C-BDE 209 Within ±70% of Opening CAL-VER for ^{13}C-BDE 209
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL) [1]
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Ion ratios must fall within ±15% of the theoretical values for positive identification of all targets in the calibration standards and samples.
Sensitivity	Minimum S:N ratio 10:1 for CS1. Minimum absolute response of BDE 209L in CAL-VER is 5 x 10^6 (Quant. + confirm. ions)
CAL-VER	Specification for BDE 209L is 25%-200% of actual concentration

[1] Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

Modifications to EPA Method 1614 (EPA-821-R-07-005, August 2007)

Sections 4.7, 7.5.3, 13.5: An anthropogenic isolation column as described in Section 7.5.3 is not used.

Sections 7.9.3: BDE 79L, BDE 180L and BDE 206L are used as injection (recovery) standards instead of PCB 52L and PCH 138L.

Section 10.4, Table 2: OcBDE and NoBDE are quantified against BDE 197L instead of BDE 209L. The retention time reference for OcBDE and NoBDE is BDE 197L instead of BDE 209L. The surrogate standards are now quantified against labelled BDE standards. The retention time references for the surrogate standards have also been changed to labelled BDE standards.

Sections 11.5.6, 11.5.8: Unless requested by the client, the aqueous portion after filtration of aqueous samples with >1% solids is not discarded but is extracted.

Section 11.5.7 Solid samples are dried by mixing with anhydrous sodium sulphate. The dried solid is extracted using a soxhlet extraction apparatus. The surrogate spike is incorporated after the drying step. The extracting solvent for solids is dichloromethane.

Section 13.1.1, 13.2: GPC chromatography, by a gravity column, is not routinely used for any matrix.

Sections 14.2, 17.5: The final extract volume is 50 µL (20 µL for blood extracts).

Section 15.3, Table 6: Changes in CAL/VER: The acceptance criterion for native BDE 209 has been changed from 50-200% to 70-130%. The acceptance criterion for BDE 209L in CAL/VER has been deleted because it is not quantified. The cleanup standard (BDE 139L) criterion is changed from 60-130% to 50-150% to be in line with the labelled surrogates.

Section 15.5, Table 6: Changes in OPR: The acceptance criterion for native BDE 209 has been narrowed from 40-200% to 50-150%. The acceptance criterion for BDE 209L has been changed from 20-200% to 10-200% and the acceptance criterion for the other labelled surrogates has been extended from 30-140% to 30-200%. The acceptance criterion for the cleanup standard (BDE 139L) is changed from 40-125% to 30-200%.

Section 16.1: Identification specification has been modified to be “signals for the two exact m/zs in Table 7 must be present and maximize within 2 seconds”.

Section 17.2, Table 6: Surrogate and cleanup standard recovery in samples: The acceptance criterion for BDE 209L has been changed from 20-200% to 10-400% and for the other surrogate standards from 25-150% to 25-200%. The acceptance criterion for the cleanup standard (BDE 139L) has been extended from 30-135% to 25-200%.

Appendix A - Semi-Quantitative Monitoring of non-BDE BFR in POTW Biosolids and Effluents

Non-BDE BFR Target Compound Suite

Abbreviation	**Full Name (**Wellington Labs Supplier)	**CA Index Name**	**CAS No.**
HBB	Hexabromobenzene	1,2,3,4,5,6-hexabromobenzene	87-82-1
PBEB	Pentabromoethylbenzene	1,2,3,4,5-pentabromo-6-ethylbenzene	85-22-3
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane	1,1'-(1,2-ethanediylbis(oxy))bis(2,4,6-tribromobenzene)	37853-59-1
DBDPE	Decabromodiphenylethane	1,1'-(1,2- ethanediyl)bis(2,3,4,5,6-pentabromobenzene)	84852-53-9

The above non-BDE BFR target compounds can be added to the routine MLA033 BDE target suite using the following additional, modified, or extended protocols:

The recommended maximum sample size is 0.1 g dry weight basis, not to exceed 0.5 grams wet.

Use of an Additional Native Standard Solution and Labelled Surrogate Standards

Authentic Analyte (Spiked to OPR)
PBEB
HBB
BTBPE
DBDPE
PBEB
HBB
Labelled Surrogate Stds (Spiked to samples and QC samples)
$^{13}C_6$-HBB
$^{13}C_{12}$-BTBPE
$^{13}C_{14}$-DBDPE

Use of an Additional Calibration Standard Solution

Calibration Standard Solution
PBEB
HBB
BTBPE
DBDPE
$^{13}C_6$-HBB
$^{13}C_{12}$–BTBPE
$^{13}C_{14}$–DBDPE
$^{13}C_{12}$-BDE-79
$^{13}C_{12}$-BDE-180
$^{13}C_{12}$-BDE-206

Modified Chromatographic Column Clean-up Procedures

Extract cleanup involves the use of layered acid base silica, alumina and Florisil chromatographic columns.

Ions to Acquire in Addition to those acquired for PBDEs in MLA-033

Compound	RT	Ion Type (M+X for Mass 1)	Func-tion	Mass 1	Mass 2	Ion Ratio m1/m2	Ion Ratio Limits (+-25%)	Quant Ref
PBEB	23.37	$[C_7H_2Br_5]+$ (M+4)	F2	484.6033	486.6012	1.03	0.77-1.29	$^{13}C_6$-HBB
HBB	25.52	$[C_6Br_5]+$ (M+4)	F2	470.5876	468.5896	1.95	1.46-2.44	$^{13}C_6$-HBB
BTBPE	38.59	$[C_{14}H_8Br_6O_2]+$ (M+6)	F4	687.5564	689.5544	1.36	1.02–1.70	$^{13}C_{12}$-BTBPE
DBDPE	53.35	$[C_{14}H_4Br_{10})$ (M+10)	F6	971.2045	973.2025	1.23	0.92-1.54	$^{13}C_{14}$-DBDPE
DBDPE *	53.35	$[C_7H_2Br_5]+$ (M+4)	*F7*	484.6033	486.6012	1.03	0.77-1.29	$^{13}C_{14}$-DBDPE
$^{13}C_6$-HBB	25.52	$[C_6Br_5]+$ (M+6)	F2	478.6057	480.6036	2.06	1.55-2.54	^{13}C-BDE-79
$^{13}C_{12}$-BTBPE	38.59	$[C_{14}H_8Br_6O_2]+$ (M+6)	F4	699.5966	701.5945	1.36	1.02–1.70	^{13}C-BDE-180
$^{13}C_{14}$-DBDPE	53.35	$[C_{14}H_4Br_{10})$ (M+10)	F6	985.2514	987.2494	1.23	0.92-1.54	^{13}C-BDE-206
$^{13}C_{14}$-DBDPE *	53.35	$[C_7H_2Br_5]+$ (M+4)	*F7*	491.6267	493.6247	1.03	0.77-1.29	^{13}C-BDE-206

* Possible alternate acquisition to increase sensitivity- requires client services specific request.

Data Accuracy and Reporting

The accuracy of this analysis has not been fully established and results are reported flagged as 'Information Values'.

Appendix H

KCEL TOC/DOC Analysis SOP

STANDARD OPERATING PROCEDURE

for

Total and Dissolved Organic Carbon (Liquid Matrix)

SOP # 03-04-001-004336v4

Date of Implementation: 01/01/2005

Supersedes SOP # 03-04-001-003

Approved by:

Author: _____ Date: _____

Supervisor: _____ Date: _____

QA Officer: _____ Date: _____

King County Environmental Laboratory
322 W. Ewing Street
Seattle WA 98119-1507

1. SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of total organic carbon (TOC) in drinking, surface, marine water, industrial and municipal wastewater, and sludges. Preliminary filtration extends application to dissolved organic carbon (DOC) in the same matrices.

1.2 The method detection limits (MDL) and the reporting detection limits (RDL) are 0.5 mg/L and 1.0 mg/L, respectively, for both TOC and DOC. The MDL and RDL for sludge samples are 500 mg/kg and 1000 mg/kg, respectively, and are based on the 1000x dilution performed when preparing the samples for analysis.

1.3 The linear range of the O-I 1020 combustion TOC analyzer, as defined by the manufacturer, is 0.5 parts per million (ppm) carbon to 5,000 ppm carbon. However, the analytical range of a routine analysis is from the MDL up to 110% of the concentration of the top calibration standard.

2. ASSOCIATED STANDARD OPERATING PROCEDURES (SOP'S)

2.1 TOC in Sediments and Soils SOP 03-04-002-002

3. METHOD SUMMARY

3.1 Addition of phosphoric acid and sparging by the instrument removes inorganic and volatile carbon from the sample. The nonpurgeable organic carbon (NPOC) remaining is converted to carbon dioxide by catalytic conversion in a heated combustion chamber packed with platinum catalyst. The carbon dioxide formed is measured directly by a non-dispersive infrared detector (NDIR). The value provides a measure of non-purgeable organic carbon in the sample. In practice, for surface and groundwaters, the purgable organic carbon is negligible, and therefore the NPOC equals TOC.

4. DEFINITIONS

4.1 Inorganic Carbon (IC) -- carbonate, bicarbonate, and dissolved CO_2.

4.2 Total Organic Carbon (TOC) -- all carbon atoms covalently bonded in organic molecules.

4.3 Dissolved Organic Carbon (DOC) -- the portion of TOC which passes through a 0.45 um filter.

4.4 Nonpurgeable Organic Carbon (NPOC) – the portion of TOC remaining in the sample after the volatile and inorganic carbon is removed by acidification and oxygen purging.

4.5 Sludge – Biosolids samples defined by the matrix Liquid Sludge (LD) in LIMS. These samples range from 1 to approximately 5% solids.

5. INTERFERENCES

5.1 Samples with particles larger than 0.1 mm in diameter may block the sample probe, and should be homogenized using a Waring blender, or filtered and analyzed as DOC. Diluting highly turbid samples prior to analysis can further reduce the affects of particulate matter on the instrument.

5.2 Saltwater could interfere with the analysis of the total carbon by fouling the catalyst, and giving an irregular peak shape and area, due to high salt content. Seawater samples that contain salt, and have the above mentioned behavior, may be diluted 2x to 5x before re-analysis to minimize catalyst problems. Operation of the 1020A at 680°C and with the chase pump on may also yield better efficiencies and recoveries for saltwater samples. Low level saltwater samples should not be diluted. The main impact of the salt is on instrument performance and analyst could minimize that by adding rinses at the end of the run and changing the catalyst if necessary.

5.3 Halogen gases can also interfere with the detector, but are removed by use of a halide scrubber, and by the selective infrared detector.

5.4 Sulfides will cause a positive TIC interference. Sulfide interference is removed by adding acid to sample and allowing to sit with lid off for at least two hours prior to analysis to drive off the interference.

5.5 Surfactants present in samples can severely damage the catalyst. The samples should be diluted in order to reduce the negative affect. If not diluted, the catalyst will have to be washed with 5% HCL and copious amounts of water before next use.

5.6 Inorganic CO_2 can interfere with the final TOC result. False, high TIC results will give low TOC results when subtracted from the NPOC. CO_2 interference is removed by allowing the sample to sit open at room temperature for at least two hours prior to analysis. The samples are also acidified and aerated during analysis to help drive off the CO_2. This is checked during analysis (see 10.5.2).

6. SAFETY

6.1 General Safety

6.1.1 All normal safety practices should be complied with including the use of lab glasses, gloves, and lab coats.

6.1.2 All samples should be treated with regard to possible toxicity and microbial potential.

6.2 Method Safety/Special Considerations

6.2.1 The furnace operates at elevated temperatures (680°C) and presents a burn hazard if not allowed to cool prior to maintenance.

6.2.2 Samples, such as sludges, with organic carbon content of 10% or more pose risk of explosion in the combustion chamber. If an unknown matrix is suspected of containing more than 10% organic carbon, dilute the sample with RO water prior to analysis.

6.2.3 Liquid samples and standards are preserved with phosphoric acid to pH<2. Care should be taken to avoid direct contact with these acidified liquids.

6.2.4 Sludge samples should be handled in the hood, especially when opening the sample container and when mixing and blending.

6.3 Chemical Handling

6.3.1 Ultrapure oxygen is used as a carrier gas. Oxygen is extremely flammable. Caution should be taken with the gas cylinder. Use only approved carts for transporting oxygen cylinders. Keep cylinders secured at all times. When loosening or tightening the regulator, always have it facing away from you.

6.3.2 10% Phosphoric acid is a diluted acid bought at this concentration from a vendor. Though not as hazardous as the concentrated solution, this reagent is still corrosive, and should be handled with caution. Gloves, eye protection and a lab coat must be used when handling this reagent. Bottles of this reagent must be stored in the acid cabinet when not in use.

6.3.3 5% Hydrochloric acid is a diluted acid bought at this concentration from a vendor. Though not as hazardous as the concentrated solution, this reagent is still corrosive, and should be handled with caution. Gloves, eye protection and a lab coat must be used when handling this reagent. Bottles of dilute hydrochloric acid must be stored in the acid cabinet when not in use.

6.4 Spill / Hazardous Waste Minimization

6.4.1 The storage and disposal of hazardous chemicals will be minimized through the laboratory's purchasing efforts. Chemicals must be purchased in the smallest possible quantities governed by the quantities available and the rate of use for the chemical. Preparing or purchasing all reagents in volumes of one liter or less where applicable minimizes spill impact. In addition, reagents should be stored in plastic rather than glass containers when possible. For more details of spill cleanup procedures see the appropriate sections in the spill cleanup SOP # 03-05-007-001.

6.5 Sample/Reagent Disposal

6.5.1 All acidified liquid samples, reagents, and standards must be disposed of in the appropriate acidic waste containers. Disposal of unprocessed samples depends on matrix; refer to Conventionals Unit Sample Disposal SOP # 03-05-006-001 and the Solid and Hazardous Sample Management SOP # 01-01-005-000.

6.5.2 Liquid waste that is generated during analysis must be disposed of in the appropriate acidic waste container.

7. SAMPLE COLLECTION, PRESERVATION AND HOLDING TIME

7.1 Samples may be grab or composite.

7.2 Recommended sample containers

7.2.1 Liquid samples

7.2.1.1 For TOC samples , two 40mL amber glass VOA vials are preferred, but 125mL high-density polyethylene (HDPE) containers are also acceptable.

7.2.1.2 For DOC samples, 125mL, amber, wide-mouthed, HDPE containers are preferred to supply an adequate amount of sample for filtration. 60 mL syringes are used for filtration to decrease the amount of handling when using smaller syringes. Samples are filtered into two 40 mL, amber glass VOA vials.

7.2.2 Sludge samples – 4 Oz, glass, soil jars or 125mL clear HDPE bottles.

7.3 The minimum sample volumes necessary for analysis are approximately 80mL for liquid samples and 10g for sludge samples.

7.4 Sample preservation

7.4.1 Phosphoric acid is the preferred preservative for TOC and DOC samples. Sample preservation with sulfuric acid is acceptable, but preservation with hydrochloric acid will adversely affect the instrument and is **not** acceptable. After preservation, samples must be stored at 4°C.

7.4.1.1 For TOC analysis, liquid samples are preserved with concentrated phosphoric acid (approximately 0.04 mLs to 40mL sample) to pH<2 as soon as possible or within one day from collection.

7.4.1.2 If DOC analysis is required, the analyst must first filter each unpreserved sample through a non-sterilized SFC 0.45µm syringe filter and then preserve the filtrate with phosphoric acid to pH<2 as soon as possible or within one day from collection/filtration.

7.4.2 Sludge samples are non-preserved, but must be stored at 4°C or frozen.

7.5 Holding times

7.5.1 For liquid samples that are properly preserved with phosphoric acid (or sulfuric acid), the holding time is 28 days.

7.5.2 Sludge samples have a holding time of 14 days at 4°C, or six months if frozen at -20°C.

8. APPARATUS, EQUIPMENT, AND CONSUMABLES

8.1 O-I Combustion TOC Analyzer, Model 1020A, with Model 1051 autosampler

8.2 Analytical Balance (Mettler AT200)

8.3 Oxygen (O_2), ultrahigh purity, 99.993% or better and <1ppm hydrocarbon (as methane) (Bryne Specialty Gas #BSG OX4.3/337)

8.4 Pre-cleaned glass vials, 40mL, amber or clear, for sample collection and autosampler tray, Fisher catalog #S246-0040 or equivalent

8.5 Waring Blender (HGBSSSS6)

8.6 Volumetric glassware for reagents and standards, class A or equivalent

8.7 Pipettes, class A volumetric or equivalent

8.8 Eppendorf or equivalent high precision pipettors

8.9 0.45µm SFCA syringe filters for DOC sample filtration (Fisher catalog #09-740-35E or equivalent). DO NOT USE STERILIZED FILTERS.

8.10 Syringe, plastic, 60mL (Fisher catalog # 1482011)

8.11 Weigh boats for weighing of sludge aliquots (Fisher catalog #NC9387722 or equivalent)

8.12 pH paper, Colorphast pH 0-14 (Fisher catalog #MN95903 or equivalent)

9. PREVENTATIVE MAINTENANCE

9.1 Daily Checks

9.1.1 Check the oxygen gas cylinder for sufficient supply daily. Replace the cylinder when the pressure drops below 500 psi.

9.1.2 Check the volume of each of the reagent reservoirs (10% H_3PO_4 and RO water). Reagent should be added to keep reservoir bottles from being completely emptied.

9.1.3 Check the water level in the humidifier vessel on the front of the instrument. Ensure that the water level is between 1/3 and ¾ full. Add RO water if necessary.

9.1.4 Check that the NDIR detector baseline reading is below 10,000. See the O-I Model 1020A Operator's Manual for the NDIR baseline adjustment procedure.

9.1.5 Check the condition of the halide scrubber. The copper shot should be replaced every four months or as necessary in the case of excessive oxidation of the copper.

9.2 Preventive Maintenance

9.2.1 The injector needle should be inspected periodically to ensure that it is properly injecting the sample into the combustion tube. If corrosive or seawater samples are analyzed routinely, this inspection should be performed weekly. See the O-I Model 1020A Operator's Manual for procedure.

9.2.2 Replace contents of the humidifier vessel weekly.

9.2.3 The sample pump tubing should be inspected after every 2000 hours of operation. See the O-I Model 1020A Operator's Manual for the tubing inspection/replacement procedure.

9.2.4 The gas permeation tube should be replaced annually as preventive maintenance. See the O-I Model 1020 Operator's Manual, page 104.

9.3 Maintenance as Needed

9.3.1 The catalyst should be conditioned prior to analysis if it has been changed, if the instrument has not been used for a long period of time, or if the integrated area counts decrease or become variable. See the O-I Model 1020A Operator's Manual for catalyst conditioning instructions, combustion tube/catalyst replacement procedure.

9.3.2 Used copper shot can be collected and cleaned in batches for reuse in the halide scrubber.

9.3.2.1 In a fume hood, add the used copper shot to a 200mL beaker.

9.3.2.2 Add approximately 20-40mL of 5% HCl to the beaker / copper shot. More concentrated acid can be used to expedite the cleaning procedure however, the acid should be no greater than 50%.

9.3.2.3 Allow the copper shot to soak for 15-20 minutes. Mixing the cooper shot will facilitate removal of the built-up oxidized material coating the copper.

9.3.2.4 Pour the contents of the beaker through a fine mesh Teflon screen, collecting the acidic waste for neutralization and disposal.

9.3.2.5 Rinse the copper shot thoroughly with RO water to remove any trace of acid.

9.3.2.6 Allow the copper shot to air dry. Nitrogen gas may be used to facilitate the drying process.

9.3.2.7 Transfer the copper shot to a clean, glass TOC vial for storage until use.

9.4 Nonscheduled Maintenance – See the O-I Model 1020A Operator's Manual for procedures for setting and testing mechanical components for proper operation if replaced during nonscheduled maintenance (troubleshooting).

10. STANDARDS AND REAGENTS

10.1 Preparation of Standards

10.1.1 Stock calibration standards (including spiking standard), and the laboratory control sample, are purchased from Environmental Resource Associates. Alternately, these standards can be prepared using Potassium Hydrogen Phthalate (also known as potassium biphthalate or KHP)**.** Dry sufficient KHP (Fisher catalog # P243-100 or Baker JT2958) overnight at 104°C; store in a desiccator prior to use.

10.1.2 All standards must be preserved with concentrated, reagent grade phosphoric acid (Fisher catalog # A242-1). Add the acid dropwise until pH<2. Check with pH paper (8.12).

10.1.3 Reagent/Standard logbook entries include concentration of the purchased or prepared standard, Prep ID (numbered in ascending order), prep date, expiration date, and preparer's initials. If preparing a stock reagent, include the chemical manufacturer, lot number, weight (in grams), and final volume of stock standard. If preparing a standard from a stock, include lot number (or prep ID) of stock, concentration of stock, volume of stock used, and final volume of standard being prepared.

10.2 Calibration Standards

10.2.1 Stock Calibration Standard, 1000 mg/L – Pre-made solution, purchased from Environmental Resource Associates, preserved with sulfuric acid (custom standard, catalog #978). Store in an amber glass bottle at 4°C for up to 1 year or as recommended by the manufacturer's date on the label. The sample is already sulfuric preserved by the manufacturer.

10.2.2 Intermediate Calibration Standard, 250 mg/L - Fill a 200mL Class A volumetric flask ½ full with RO water. Add 50.0mL of 1000 mg/L Stock Calibration Standard (10.2.1) using a Class A volumetric pipette. Preserve with approximately 10 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water, stopper and mix well then verify <2 pH. Store in a HDPE bottle at 4°C for up to 2 months.

10.2.3 Curve Extension Standard (Std6), 50 mg/L – Fill a 100mL Class A volumetric flask ¾ full with RO water. Add 5.0mL of 1000 mg/L Stock Calibration Standard (10.2.1) using a Class A volumetric pipette. Preserve with approximately 5 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water, stopper and mix well, then verify <2 pH. Store in a HDPE bottle at 4°C for up to 2 months.

10.2.4 Calibration Standard (Std5), 25 mg/L – Fill a 250mL Class A volumetric flask ¾ full with RO water. Add 25.0mL of 250mg/L Intermediate Calibration Standard (10.2.2) using a Class A volumetric pipette. Preserve with approximately 10 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water, stopper and mix well, then verify <2 pH. Store in a HDPE bottle at 4°C for up to 1 month.

10.2.5 Calibration Standard (Std4/CCV), 10 mg/L – Fill a 500mL Class A volumetric flask ¾ full with RO water. Add 20.0mL of 250mg/L Intermediate Calibration Standard (10.2.2) using a Class A volumetric pipette. Preserve with approximately 20 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water, stopper and mix well, then verify <2 pH. Store in a HDPE bottle at 4°C for up to 2 weeks.

10.2.6 Calibration Standard (Std3), 5 mg/L – Fill a 250mL Class A volumetric flask ¾ full with RO water. Add 5.0mL of 250mg/L Intermediate Calibration Standard (10.2.2) with a Class A volumetric pipette. Preserve with approximately 10 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water; stopper and mix well, then verify <2 pH. Store in a HDPE bottle at 4°C for up to 1 week.

10.2.7 Calibration Standard (Std2/RDL), 1 mg/L – Fill a 250mL Class A volumetric flask ¾ full with RO water. Add 1.0mL of 250mg/L Intermediate Calibration Standard (10.2.2) with a Class A volumetric pipette. Preserve with approximately 10 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water; stopper and mix well, then verify <2 pH. Store in a HDPE bottle at 4°C for up to 48 hours.

10.2.8 Calibration Standard (Std1), 0 mg/L – Fill a 500mL Class A volumetric flask with RO water. Preserve with approximately 20 drops of concentrated phosphoric acid (10.1.2), stopper and mix well, then verify <2 pH. Store at 4°C. Store in a HDPE bottle at 4°C for up to one week.

10.3 Spiking Standards

10.3.1 Primary Spike Solution, 1000 mg/L – Same solution as what is listed in 10.2.1.

10.4 Laboratory Control Standard (LCS)

10.4.1 Stock LCS Standard, 1000mg/L – Pre-made solution, purchased from Environmental Resource Associates, preserved with sulfuric acid (custom standard, catalog #978). Store in an amber glass bottle at 4°C for up to 1 year as recommended by the manufacturer's date on the label. The sample is already sulfuric preserved by the manufacturer. This solution must be from a different lot # than that of the solution used for the stock calibration (10.2.1).

10.4.2 Working LCS 10.0 mg/L – Fill a 500mL Class A volumetric flask ¾ full with RO water. Add 5.0mL of 1000mg/L Stock LCS Standard (10.4.1) using a Class A volumetric pipette. Preserve with approximately 20 drops of concentrated phosphoric acid (10.1.2), dilute to the mark with RO water, stopper and mix well, then verify <2 pH. Store in a HDPE bottle at 4°C for up to 2 weeks.

10.5 Total Inorganic Carbon Standards (TIC) and CCV TIC Check

10.5.1 Stock Calibration Standard, 1000mg/L. Fill a 250 mL Class A volumetric flask 2/3 full with RO water and add 2.205 g of dried Na_2CO_3. Dilute to mark with RO water, stopper and mix well. Store in a clear HDPE bottle at 4°C for up to 3 weeks. Do NOT preserve. If a calibration curve needs to be run for TIC only, make serial dilutions from this 1000 mg/L solution to obtain the same concentrations used for the TC calibration curve.

10.5.2 CCV TIC Check – This standard is run once at the beginning of each analytical run. It is used to verify that the PAM module is sufficiently removing IC from solution. The standard consists of 35mL of the std4 (10 mg/L) spiked with 350uL of the 1000 mg/L IC standard (10.5.1) providing a final Total Carbon concentration of 20 mg/L, 10 mg/L of which exists as IC. Analysis should provide a result of 10 mg/L if all IC has been successfully removed. If the actual value is greater than 110% of this, cap and agitate the samples and allow the samples to sit out longer (a minimum of one hour) to drive off the CO_2 before restarting the analysis.

10.6 Reagents

10.6.1 Phosphoric Acid (H_3PO_4), 85% - Purchase reagent grade, concentrated phosphoric acid (85%) from Fisher, catalog #A242-1. The solution should be stored in the acid cabinet. The manufacturer's recommended expiration date should be followed, which is usually two years past the date of production.

10.6.2 Phosphoric Acid (H_3PO_4), 10% - Purchase from Fisher, catalog #LC18650-2. Alternately, prepare this reagent in the hood. Fill a 1000mL Class A volumetric flask about ½ full with RO water. Carefully add 118mL concentrated phosphoric acid (10.6.1) to the flask. Mix, cool, and dilute to the mark with RO water. Store in a clear HDPE bottle at room temperature for up to 3 months. Dispose of this reagent in an acidic waste container.

10.6.3 Hydrochloric Acid (HCl), 5% - Purchase from Fisher, catalog #LC15050-2. Alternately, prepare this reagent in the hood. Fill a 1000mL Class A volumetric flask about ¾ full with RO water. Carefully add 50mL concentrated hydrochloric acid to the flask. Mix, cool, and dilute to the mark with RO water. Store in a clear HDPE bottle at room temperature for up to 3 months. Dispose of this reagent in an acidic waste container.

10.6.4 Reverse Osmosis (RO) Water – carbon-free, ASTM Type I

11. PROCEDURE

11.1 Method Blank Preparation

11.1.1 For TOC, prepare the method blank by preserving 500mL RO water with approximately 20 drops of concentrated phosphoric acid (10.6.1) then verify <2 pH. The method blank should be freshly prepared with each analytical run.

11.1.2 If DOC analysis is required, prepare the method blank by filtering a portion of RO water through a non-sterilized SFCA 0.45µm syringe filter prior to preservation.

11.1.3 For Sludge TOC, add 500mL RO water to blender and mix for 2 to 3 minutes. Preserve with approximately 20 drops of concentrated phosphoric acid (10.6.1) then verify <2 pH.

11.2 Sample Preparation

11.2.1 Dissolved Organic Carbon (DOC) - Filter sufficient volume of unpreserved sample through a non-sterilized SFCA 0.45µm syringe filter (8.9) into two 40mL amber glass VOA vials. Samples

must be filtered as soon as possible or within one day of sampling. Filtered aliquots are preserved with concentrated phosphoric (approximately 0. 04mL to 40mL of sample) acid to pH<2 immediately following filtration step. Spot checking random samples from the filtration batch is used to verify preservation. A minimum of 1 in10 (10%) of the preserved samples are checked using pH strips to verify the pH is <2. Record the filtered samples in the Analysis/Preparation Logbook (13.3.1). Filtered method blanks should be prepared at the same time at a rate of one-per-twenty samples and analyzed with the samples.

11.2.2 Total Organic Carbon (TOC) - Mix sample well prior to analysis. If high turbidity is present, dilute sample to prevent clogging of instrument lines. Dilutions including sample volume and amount of dilution water should be recorded in the analysis logbook. Adjust detection limits accordingly. Stir bars are also added to each vial to ensure complete homogenization.

11.2.3 Sludge samples

11.2.3.1 Prepare sludge samples on the day they are to be analyzed. Open the sludge calculation worksheet template. Go to K:/conventi/Qamanual/Analytic/TOCSludgeCalcSheet.xlt. Save as TOCSludgeCalcSheetYYMMDD.xls where YYMMDD is the year, month and day of the blending and analysis.

11.2.3.2 Mix sludge sample thoroughly in the hood. Weigh about 0.5g of the sludge into a small weigh boat. On the spreadsheet record sample number, sample weight in grams and the volume of RO water used (usually 500mL).

11.2.3.3 Add the weighed sludge to Waring blender along with 500mL RO water. Blend for 3 to 4 minutes (in the hood). Pour the blended sample into a labeled, 500mL HDPE jar. Transfer 30mL of each blended sludge sample into a clean, labeled 40mL glass vial, preserve with approximately 0.1mL concentrated phosphoric acid and verify a pH<2. Add a stir bar, cap the sample vial and set aside for subsequent analysis. In most cases, no more dilution is necessary.

11.3 Laboratory duplicate (LD) preparation – Repeat the procedure described above in 11.2.3.2 and 11.2.3.3 for the LD preparation.

11.4 Matrix spike (MS) preparation

11.4.1 TOC and DOC – Mix and measure 35mL of the sample to be spiked in a clean, 50mL graduated cylinder. Pour the measured sample into a clean, labeled 40mL glass vial. Add 0.35mL of Primary Spike Solution (10.3.1) to the glass vial, cap, and mix. The true value of the spike is 10mg/L.

11.4.2 Sludge samples – Mix and measure 30mL of the blended sludge sample to be spiked in a clean, 50mL graduated cylinder. Pour the measured sample into a clean, labeled 40mL glass vial. Add 0.60mL of Primary Spike Solution (10.3.1) to the glass vial. Cap, mix, and set aside for subsequent analysis. The true value of the spike is 20mg/L.

11.5 Choice of Calibration Standards

11.5.1 The five calibration standards used to generate a typical calibration curve for the 1020A are an aliquot of each of the standards found in 10.2.4 through 10.2.8.

11.5.1.1 The linear range of an analytical run is from the matrix's MDL up to 110% of the concentration of the top calibration standard. The analytical range can be extended by running a higher concentration standard (must be within 10% of true value) to show linearity of the curve to 110% of that concentration. Std6, 10.2.3 may be used to extend linearity.

11.5.1.2 If a sample is greater than the curve and the extender, it will be necessary to dilute the sample accordingly with RO water. The analyzer will give a rough estimate of the result even when above the calibration curve, which can be used to guide the dilution factor. Any dilutions should be noted in the analysis logbook (13.3.1), and also on the sample table next to the sample ID. Any sample analyzed as a dilution must be designated as **Run Type** "*Check Standard*" on the sample table. This is necessary to correct the associated data for the background response of the RO water used to make the dilution. See section 11.12.6.7 for details on **Run Type** designations.

11.6 Continuing Calibration Verification (CCV) – The calibration standard, near the middle of the range of the calibration curve (Std 4, 10.2.5), is run as a CCV directly after the calibration curve, after every 10 samples during the analytical run, and at the end of the run.

11.7 Reporting Detection Limit Check (RDL) – The calibration standard at the RDL (Std 2, 10.2.7) is analyzed at the beginning of each analytical batch, usually directly after the first CCV.

11.8 Method Blank (MB) – A method blank (11.1.1) is analyzed once at the beginning of each analytical batch (usually directly after the RDL check), and once per 20 samples.

11.9 Laboratory Control Sample (LCS) – An LCS is analyzed once at the beginning of each analytical batch (usually directly after the MB), and once per 20 samples. Use the working LCS that is at or near the midpoint of the calibration range (10.4.2). A DOC LCS requires filtration through a non-sterilized 0.45 µm SFCA syringe filter (8.9) prior to analysis.

11.10 Spike Blank (SB) – A SB is analyzed with each analytical batch, and preparation should coincide with matrix spike sample preparation. Measure 35 mL of the prepared method blank and pour in a clean 40mL amber VOA vial. Add 0.35 mL of the Primary Spike Solution (10.3.1) to the 40mL VOA vial. The true value of the spike is 10 mg/L. A DOC SB requires filtration of the prepared method blank solution through a non-sterilized 0.45 µm SFCA syringe filter (8.9) prior to spiking.

11.11 Instrument Startup

11.11.1 Turn on the oxygen gas to 60 psi.

11.11.2 Turn on the power switch on the right back panel of the instrument. Also, turn on the power switch on the left back panel of the 1051 autosampler.

11.11.3 During the TOC Analyzer's boot-up, a series of audible beeps will indicate the status of the instrument.

11.11.3.1 One beep indicates system startup.

11.11.3.2 Two beeps indicate the CMOS check passed.

11.11.3.3 Three beeps indicate that the firmware is ready to start WinTOC communication.

11.11.4 After the three beeps sound, Select Start/Programs/OI Analytical/TOC 1020A/WinTOC 1020A System 1.

11.11.5 Create the sequence for the analytical batch.

11.11.5.1 To access the sequences screen, go to the **Databases** menu and choose **Sequences**.

11.11.5.2 The **sequences** screen provides access to the loaded sequence. Seven lines of the sequence are displayed at the top of the screen and include **Position/Vial #, Sample Name**, **Method**, **Run Type**, **Replicates**, and **Use Outlier Removal** option.

11.11.5.3 At the bottom of the sequences screen, choose **Open** and select the appropriate sequence template. Next, at the bottom of the sequences screen, choose **Save As** and enter today's date, using the naming convention MMDDYY, where MMDDYY is today's date (month, day, and year).

Note: A pre-acidification and purging process is performed for both TOC and TC sequences to remove inorganic carbon (IC) in the sample. The difference between the TOC and TC sequence is that total inorganic carbon (TIC) determination is performed with the TOC sequence to evaluate TIC level in the sample. The TC sequence is only used for sample with amounts of IC known to be less than the MDL.

11.11.5.4 Select the sequence line by clicking with the mouse in the **Sample Name** field. Change the name by typing characters.

11.11.5.5 Use the mouse or tab key to move among fields.

11.11.5.6 The **Method** of the analysis can be selected by typing the name or by using the pulldown menu at the right of the field. It is possible to use different methods with different samples. The default method used is **KCEL1**. If the method name is **unknown**, that position will not be analyzed.

11.11.5.7 Each position on the sample tray must be designated by the Run **Type** of the solution in the sample vial. The software only allows designations of *"Standard, "Check Standard"*, or *"Sample"*. The different designations allow the software to treat the analysis output differently (See Calculations 13.1.2 and 13.1.3). For *Standards* and *Check Standards*, the background response of the RO water used to prepare these solutions is automatically subtracted. This response is not automatically subtracted whenever a position is designated as *Sample*.

11.11.5.7.1 *Standard* is used for each calibration standard, choosing Std 1 through Std 5 for standards, in order of low to high-level.

11.11.5.7.2 *Check standard* is used for all non-specific matrix QC such as MB, RDL, LCS, SB, CCV TIC Check, Curve extender check (50ppm), and CCV's. This is also used for any sample analyzed at a dilution, and sludges.

11.11.5.7.3 *Sample* is used for all samples and other specific matrix QC, such as Laboratory Duplicates and Matrix Spikes that are not analyzed at dilutions.

11.11.5.8 If any comments need be associated with the position to be analyzed (*sample, standard, or check standard*), a remark may be entered in the **Remarks** field.

11.11.5.9 Enter the number of **Replicates** for the sample. The initial Baseline sample is run at least four times, before the Calibration Standards, which are analyzed at least three times. Samples, and other QC are run in at least duplicate. This value can increase based upon the RPD% between samplings as specified in the User Outlier Removal process.

11.11.5.10 Select **User Outlier Removal** to automatically verify the relative standard deviation or the standard deviation as less than the required percentage. If the calculated %RSD values is greater than the set limit, and **Max Reps** is set greater than **Reps**, another replicate analysis will be performed and the values compared to the limit again. Currently, five is the maximum number of replicates performed if the %RSD criteria are not met. The operator can select what action should occur (continue, abort, or prompt) if the values do not fall below the required percentage before the maximum number of replicates has been run. Current protocols are to continue the analysis, and return to the sample in question at a later analysis or the end of the current one.

11.11.5.10.1 Samples - Currently, a %RSD of less than 10% is the required setting for samples.

11.11.5.10.2 Standards – Currently, 10% is the required setting for the 0mg/L, 1mg/L and 5mg/L standards. Five percent is the required limit for the 10mg/L and 25 mg/L standards. Tighter limits are used at the higher standards levels due to the effects on the low end of the curve that can result with variability at the higher end of the calibration range.

11.11.5.11 Select the **Mode** for each sample: TIC, TC, or TOC. All standards, MBs, RDLs, and LCSs should be run as TC. The amount of TIC will be much lower than the MDL, and therefore, TC may just be analyzed. All samples that are not associated with routine KCELs (King County Environmental laboratory) monitoring programs, *must* be run as TOC. Routine monitoring programs are those for which the historical data have confirmed that the TIC component of the samples are consistently below the method detection limit. The projects currently fitting this definition include Major Lakes (421235), Streams (421240, 423258), and Green Duwamish (423550-200).

11.11.5.12 When the sequence is entered completely, click on **Clear Lines** in the upper right-hand corner of the sequences screen. Clear all lines after your sequence down to line 88.

11.11.5.13 Click **Save As** to save the sequence (MMDDYY) and **OK** to exit the sequences screen.

11.11.5.14 Enter the samples included in the sequence in the Analysis/Preparation Logbook (13.3.1), along with any pertinent information relating to the samples (i.e. dilution, notable observances, etc.).

11.11.6 Go to the **Setup** pulldown menu and click on **Configuration**. Check the configuration screen and update if necessary. The settings should be as follows.

Sample Introduction – Autosampler.

Furnace Set – 680°C.

Sample Loop – 202µL loop (may vary slightly depending on the sample loop used)

Autosampler Options – 53 vial tray, Preacidification.

Sample Needle Depth – 93%.

Wash Needle Depth – 95%.

Preacid Volume – 1000µL.

Preacid Purge Time – 3 minutes.

11.11.7 Go to the **Setup** pulldown menu and click on **WinTOC Output**. Update the WinTOC Output screen. The settings should be as follows.

Report to Windows Printer.

At end of Sequence.

Report to Screen.

Base Directory: C:\WINTOC\DATA20

Subdirectory: YYMM (today's year and month).

Run Log File Name: YYMMDDMonth, Day, Year of analysis).

Report to File: Prefix/Counter

Prefix: DD (day of analysis).

Counter: Set to 101 at the beginning of the day.

Operator: Analyst's initials.

Run Log Header Options: All set to full, except:
Result: Tabular/S.

11.11.8 If a new calibration curve is needed prior to analysis then see 11.5. If not then see 11.12.9.

11.11.9 Go to the **Instrument** pulldown screen and click on **Calibration**. At the bottom of the calibration screen, click on **Open**, select **calib.temp** for new calibration template**,** and click on**Save As**. Update the calibration name, using the naming convention MMDDYY, where MMDDYY is today's date (Month, Day, Year). If using an existing curve, open the curve for that day. The curve will automatically be loaded for the sequence being analyzed. As each new calibration standard is analyzed during the run, it will replace the results saved previously. A calibration curve may be used for an entire week, if the instrument is not adjusted or turned off, and the gases and reagents are not changed. The calibration curve is different from the sequence made for the sample table. The LCS should have a recovery of 85 to 115%, and CCV recovery of 90 to 110% in order to continue using the existing calibration curve. If not acceptable, a new calibration curve should be created and analyzed for that day.

11.12 Liquid Sample Analysis

11.12.1 Loading the autosampler carousel.

11.12.1.1 Remove the carousel cover and gently lift and pull out the autosampler carousel.

11.12.1.2 Rinse each blank, calibration standard, LCS, SB, TIC CCV Check, and CCV vial several times with RO water, or use new pre-cleaned 40mL vials (8.4). Label each vial if necessary. Add the appropriate blank or standard to each vial, leaving ½ to 1 inch headspace to allow acid addition and mixing during analysis. Place each QC vial onto the autosampler carousel in the appropriate numbered spot, according to the current sample sequence.

11.12.1.3 If analyzing blended sludge samples, set the capped sample vials aside to be added to the sample carousel later, to minimize settling before analysis.

11.12.1.4 For all other samples, invert the first sample vial several times, remove the septum cap, and quickly remove the top ½ to 1 inch of sample (if necessary) to allow for acid addition and mixing during analysis. Recap and invert the sample several times again. Remove the cap and place sample on the tray in order determined by the sequence assigned. Repeat the procedure for each of the rest of the vials to be analyzed.

11.12.1.5 Place each sample vial onto the autosampler carousel in the appropriate numbered spot, according to the current sample sequence.

11.12.1.6 Place a small, rinsed stir bar into each sample vial to be analyzed.

11.12.1.7 Gently slide the autosampler carousel back into the autosampler, lining up the notch so that the first vial is in front. Replace the carousel cover.

11.12.1.8 TOC samples should sit in the autosampler carousel inside the instrument for about 2 hours to help facilitate IC removal from the samples prior to analysis (not necessary for sludge samples). The removal if IC can also be expedited by capping and shaking the samples several times over the course of an hour.

11.12.2 Check for stable baseline by checking the IR signal and the output graph on the status screen. The IR signal should be below 10,000. If not, the IR baseline should be adjusted. See the O-I Model 1020A Operator's Manual for the NDIR baseline adjustment procedure.

11.12.3 Select **Start** on the status screen to start running the sequence.

11.12.4 Monitor the calibration standards, MB, RDL, SB, LCS, and CCV TIC Check for data quality. Also monitor CCV's for calibration verification during the run.

11.12.5 If analyzing blended sludge samples

11.12.5.1 Wait until the calibration curve has been analyzed.

11.12.5.2 See 11.2.3.3. Be sure to invert each sludge vial several times, remove the cap, add a small stir bar to each vial, and add to the autosampler tray when prompted by the software.

11.12.6 To change the sequence and to add vials during analysis.

11.12.6.1 Access the sequences screen. Go to the **Databases** menu and choose **Sequences**. Click on one of the lines of the sequence. Edit sequence if necessary. Exit the **Sequences** screen by pressing **OK**.

11.12.6.2 When the instrument is finished with the sample it is currently analyzing, it will pause, spin the carousel tray to the front of the instrument, and a prompt will appear on the computer screen that says "Adjust autosampler vials and click OK to continue the sequence."

11.12.6.3 Remove the autosampler tray and place the new vial(s) in their respective numbered spots on the tray.

11.12.6.4 Gently slide the autosampler tray back onto the carousel, lining up the notch so that the first vial is in front. Replace the carousel cover. Click **OK** to resume the sequence.

11.12.7 LapLink software may be used to monitor your analytical run from another computer. See the LapLink user's manual for instructions. **NOTE: Do not run LapLink for more than 24 hours at a time or the software may cause your computer to freeze. Close application daily.**

11.12.8 Replicate NPOC analysis is performed for each sample, and the average of the two results is reported.

11.12.9 The analytical range of the analytical run is from the matrix's MDL up to 110% of the concentration of the top calibration standard. Samples outside this range must either be diluted and re-analyzed at the same range, or the instrument may be re-calibrated at a higher range and the samples rerun accordingly, along with the proper QC.

11.12.10 To stop all runs on this instrument, press **Abort**.

11.13 Shutting Down the Instrument

11.13.1 Close the WinTOC software.

11.13.2 Turn off the power switches on the 1020A and the 1051 autosampler.

11.13.3 Allow the instrument to cool for at least 20 minutes with the oxygen gas flowing.

11.13.4 Turn off the oxygen gas at the tank.

11.13.5 If using the same curve for the week, leave the instrument on without shutting it off. One tank of oxygen should be sufficient to get through one week of continual use.

11.14 Remove analyzed samples and standards from the autosampler carousel.

11.14.1 Remove the carousel cover and gently lift and pull out the autosampler carousel.

11.14.2 Use a large stir bar to pull the small stir bars out of each vial, without compromising the remaining sample. From the outside of the vial, slide a large stir bar from the bottom up to the top and directly above the vial. Save the stir bars for reuse.

11.14.3 For each sample, replace the septum cap and mark the cap to show that the vial has been analyzed. Return the analyzed sample vials to the refrigerator for storage at 4°C.

11.14.4 For each blank or standard, dispose of the remaining acidified liquid (6.5.1), replace the septum cap, and place the empty vial in a rack for use in the next analytical run. See 11.13.1.2.

12. QA/QC REQUIREMENTS

12.1 Calibration

12.1.1 The calibration curve is valid for up to one week. A new calibration curve must be redeveloped if CCV1 recovery is outside the 90-110% control limit.

12.1.2 Coefficient of Correlation - The coefficient of correlation (r-square) for the standard curve must be 0.995 or higher. If the value is less than 0.995, abort the run and restart the sequence to reanalyze the calibration standards. If still out of control, remake standards and reanalyze calibration curve. If still out of control, check with a senior chemist or your supervisor.

12.1.3 Continuous Calibration Verification (CCV) - Continuous calibration verification standards are analyzed before and after every 10 samples.Std4, 10.2.5 is used . Recoveries are expected to be within 90 to 110% of true value. If a CCV is out of control, stop the run and troubleshoot before re-analysis. Samples bracketing the failed CCV should be re-analyzed prior to reporting to LIMS.

12.1.4 Reporting Detection Limit Check (RDL) – An internally prepared standard at or near the RDL is analyzed at the beginning of each analytical batch following the calibration. This check standard is not used for reporting purposes, but is a qualitative indicator of the method and the instrument performance.

12.1.5 Analytical Range – The analytical range is from the MDL to 110% of the highest calibration standard. Samples with concentrations greater than 110% of the highest calibration standard must either be diluted and reanalyzed, or the analytical range may be extended. The analytical range can be extended by the analysis of a standard of known concentration above the normal range. The curve can be considered linear up to the concentration of this standard if the calculated value is within 10% of the true value.

12.2 Method QC

12.2.1 Method Blank (MB) – Method blanks are analyzed at a frequency of at least one per 20 samples. If a method blank is above the method detection limit (MDL), any samples less than 10 times the detected amount in the detected method blank are considered affected and reanalysis of the blank is required. If still above MDL, and there is enough sample for re-analysis, recalibrate with fresh calibration standards and re analyze. If still above MDL, LIMS will qualify all samples which are less than ten times that blank value.

12.2.2 Spike Blank (SB) – Spike blanks are analyzed at a frequency of one per analytical batch. The recovery is expected to be within 80 – 120% of the true value. Routine spike concentration is 10mg/L. However, the spike amount added should be between 2-5 times the concentration of the spiked sample. If the SB is out of control, remake and re-analyze. If not possible to re analyze, evaluate all QC samples in the batch, and discuss with supervisor before taking additional corrective action steps.

12.2.3 Laboratory Control Standard (LCS) – Laboratory control standards, at or near the midpoint of the calibrated range, are analyzed at a frequency of one per 20 samples. Recovery is expected to be within 85 to 115% of the true value. If the LCS is out of control, reanalyze same aliquot, and prepare and analyze a fresh aliquot. If still out of control, prepare fresh calibration standards, recalibrate, and rerun all samples. If still out of control, check with a senior analyst and/or your supervisor.

12.3 Matrix QC

12.3.1 Laboratory Duplicates (LD) – Laboratory duplicates are analyzed at a frequency of one per 20 samples per matrix. Samples selected for laboratory duplicates should be representative of the matrix. The absolute value of the relative percent difference (RPD) should be ≤ 20%. If laboratory duplicates are out of control, check that the samples were not mixed up. If both results are below the RDL, then no corrective action need be taken. If still out of control, repeat analysis of sample and laboratory duplicate. Check with a senior analyst and/or your supervisor if the laboratory duplicate is still out of control.

12.3.2 Matrix Spikes (MS) – Matrix spikes are analyzed at a frequency of one per 20 samples per matrix, and the recovery based on the sample should be 75 to 125%. For sludges, the spike recovery acceptance window is 70-130%. Ideally, samples are spiked at a level 2-5 times of the expected

sample value. If the matrix spike is out of control, check that the samples were not mixed up, repeat analysis of the sample and matrix spike, evaluate level of spike amount added and review SB and LCS recoveries. Check with a senior analyst and/or your supervisor if the matrix spike is still out of control after re analysis.

12.4 MDL Studies and Validation Procedures – A minimum of a one day method detection limit study is performed on a yearly basis to verify the existing detection limits. A three day (non-consecutive) MDL study may be required to (re)establish an appropriate MDL following major methodology modifications. Each day of a MDL Study consists of analyzing seven replicates of a standard at or near the reporting detection limit (2-5X the MDL) of each analyte. The concentrations analyzed for TOC are 1.0 mg/L and 2.0 mg/L. See the Quality Assurance Manual Appendix E, section B for details on MDL determination. Hardcopies of the calculated MDLs and raw data are maintained in the conventionals lab within the "MDL Studies" cabinet. See section Appendix H of the Quality Assurance Manual for further detail on method validation criteria.

13. DATA REDUCTION, REPORTING, REVIEW AND DOCUMENTATION

13.1 Calculations

13.1.1 The O-I 1020A software will automatically calculate the concentration (in mg/L C) of the samples analyzed, and then average the acceptable aliquots analyzed. The software will also correct for dilutions if the dilutions are indicated in the sample ID of the Sample Name field. See 11.12.5.4.

13.1.2 If sludge samples have been analyzed, the sludge calculation worksheet (11.2.3.1) will be necessary to complete the calculations. On the worksheet, enter the instrument result for each sample. See 13.2.1. The sample number, sample weight, and volume of RO water used for each sludge sample should already have been entered (11.2.3.2). Enter the DI blank result to account for the background TOC in the RO water used to dilute the sludge samples. See 13.1.3. The worksheet will calculate the DI-adjusted instrument result. The worksheet takes into account any further dilutions performed on the sludge samples, and then multiplies the DI-adjusted instrument result by the volume of RO water used (in mL), then divides by the sample weight used (in grams) to get the sample result in mg/kg.

13.1.3 The O-I 1020A software automatically blank-corrects results of any analyses that have been type-designated (11.12.5.7) as standard and check standard, based on the analytical result of Std 1. The blank correction subtracts out background TOC contributed by the RO water used to prepare each calibration and check standard, resulting in a true TOC concentration for each standard. No blank correction is performed on any analytes that have been type-designated as sample.

13.2 Data Reporting

13.2.1 Conversion of Raw Data to *.csv file

13.2.1.1 Go to the Utilities pulldown menu and click on Reporting to use TOC Reporter.

13.2.1.2 To open sample files in TOC Reporter, go to the File pulldown menu and click on Open. Find the first 15 files from the analytical run (the software is limited to a maximum of 15 files). For example, for the run from March 1, 2000, you want folder C:\Wt_1020a\Data20\0300\030100. Next, click on yymmdd101.RLT and drag down to yymmdd115.RLT, highlighting the files. Click OK.

13.2.1.3 To export sample files, go to the Analysis pulldown menu and click on Statistics. Click on the Export button, and using Comma as the column delimiter, click on OK. Save the group of exported files on the K drive. For our example, save to folder K:\conventi\TOC_Raw_Data\Liquid. Save the file using the naming convention MMDD# where “MM” is the month, “DD” is the day of the data collection, and # represents the data file extension starting with A then B, C etc.. On the statistics screen, click on OK.

13.2.1.4 To close sample files in TOC Reporter, go to the File pulldown menu and click on Close. For our example, highlight yymmdd101.rlt to yymmdd115.rlt, and click OK.

13.2.1.5 To export more sample files using TOC Reporter, repeat the above procedure (13.2.1.2 through 13.2.1.4). For our example, you would save the next batch of 15 files in 0301b.csv, and so on.

13.2.1.6 To convert the data to one *.csv file for our example, open Excel and access the "TOC Data File Selection" form. To access this form, open Excel and from the CON Data Entry/Reduction select Demands>>Total Organic Carbon>>Reporting/Formatting.

13.2.1.7 On the "TOC Data File Selection" form, enter the root data file name (i.e. MMDD) select the "Liquid" matrix class, and select the applicable file extensions (i.e. A, B, C, etc.) before clicking "OK".

13.2.1.8 On the "Formatted_Data" worksheet, select all results under "Reported Value" column except for CCVs and Press "Mark Samples" on the Conventionals Menu bar to highlight the results.

13.2.1.9 Next, go to the CON Data Entry/Reduction Menu select Demands>>Total Organic Carbon>>CSV Routine (Liquids). At "Product Selection" select TOC or DOC and click the "Select"button to create the CSV file.

13.2.1.10 Then save the file as MMDDL_WGXXXXX, where MMDDL is the month, day, the letter is the sequential run of the day and WGXXXXX is the workgroup number.

13.2.1.11 If DOC was requested, go to K/Conventi/Data_Review/TOC_Data_Review, and use the "Data Review" button on the Conventionals tool bar to generate a TOC vs. DOC graph. The TOC's should be greater than the DOC, this graph will quickly show you if any results need to be checked. In most cases TOC > DOC. On some occasions, they are the same, or the DOC is slightly higher. If the discrepancy is less than the MDL or the calculated RPD value for the two results is less than 20%, the result is okay. If higher, it may be necessary to re-analyze the aliquot for both chemistries again. Include this sheet in the final data package.

13.2.1.12 If sludge samples were analyzed, you must substitute the final result (in mg/kg) for each sample from the sludge calculation worksheet (13.1.2).

13.2.2 LIMS Data Entry

13.2.2.1 Results are to be entered on an ""as received"" basis (i.e., corrected for dilutions but not for dry weight) using the listid CVTOC for Total Organic Carbon and CVDOC for Dissolved Organic Carbon.

13.2.2.2 Open the CSV file in Excel format and use the "Load LIMS" button on the CNV Data Tool bar to load the file to LIMS.

13.2.2.3 The LIMS calculation will apply significant figures logic, rounding to three figures above the RDL, 2 figures between the MDL and RDL, and below the MDL no figures will be reported.

13.2.3 Data Package - The data package should include the workgroup review sheet, workgroup report, Seedpak3 data report, the instrument printout from the run (including the sample sequence and results), calibration curve graph and statistics, combined page of downloads from TOC Reporter, the *.csv file, and the Seedpak3 QC Report. A Corrective Action Form and/or a Sample Receipt Record form should also be included if necessary. Also, include copies of the sludge calculation worksheet and/or the TOC dilution calculation worksheet if applicable, and a copy of the DOC Analysis/Prep sheet if used.

13.3 Documentation

13.3.1 TOC/DOC Total Organic Carbon and Dissolved Organic Carbon Analysis Logbook for Liquid Matrix Samples-This logbook consists of three different sections all pertaining to preparation and analysis.

13.3.1.1 The first section should include all specific information requested (ie… date, analyst, sample ID, …), all analytical observations encountered (ie…calibration information, QC evaluation, analytical anomalies…), and all corrective action performed during the analytical run.

13.3.1.2 The middle section is labeled DOC Filtration and Preparation. Whenever a sample is filtered for DOC, entries are made in the logbook relating to that particular batch include the date, analyst's initials, project number, associated filtered QC, and cooler identification samples are stored in, as well as any comments concerning the filtration process.

13.3.1.3 The last section is the Instrument Logbook – Whenever a repair or maintenance is performed, an entry is made. Include the analyst's initials, date, instrument anomaly, action performed, and resolution. Include details about instrument performance before and after corrective action and any anomalies or other observations about an analytical run. Include specific maintenance details if appropriate.

13.3.1.4 Reagent/Standard Logbook – Every time a reagent or a standard is prepared, it must be documented in the reagent/standard logbook. Reagent/Standard logbook entries include concentration of standard being prepared, Prep ID (numbered in ascending order), prep date, expiration date, and initials. If preparing a stock reagent, include the chemical manufacturer, lot number, weight (in grams), and final volume of stock standard. If preparing a standard from a stock, include the prep ID or lot number (if preparing from a purchased stock), concentration of stock, volume of stock used, and final volume of standard being prepared.

14. REFERENCES

14.1 Standard Methods for the Examination of Water and Wastewater 20th ed., Method 5310B, Combustion-Infrared Method.

14.2 EPA Methods for the Chemical Analysis of Water and Wastes, 415.1.

14.3 O-I Analytical Model 1020 Combustion Total Organic Carbon Analyzer Operator's Manual.

14.4 O-I Analytical Model 1051 Vial Autosampler Operator's Manual.

15. TRAINING

15.1 The steps followed for training a new analyst is to demonstrate the preparation and analysis of total and dissolved organic carbon on samples, explaining each step of the procedure, and using the SOP as an aid. The analyst-in-training then prepares samples, performs routine maintenance on the instrument, and analyzes samples while being observed by the trainer, who answers questions, provides feedback on technique and further explains the steps in the procedure. The trainer continues to observe the analyst-in-training on a daily basis until both are comfortable that the new analyst is competent to perform the procedure. All personnel preparing and analyzing samples for total and dissolved organic carbon will be fully trained by an experienced analyst.

15.2 All training is documented using the Conventional Section Cross-Training Guidelines Check Sheet. This sheet outlines the major issues that must be addressed in order to complete the training. This sheet documents who was involved in the training and when specific aspects of the training were completed. The completed check sheet is maintained on file by the supervisor.

15.3 In order to complete the training, the trainee must analyze a set of blind samples prepared by the trainer. Upon successful analysis of the blind samples, a complete data package including instrument report and a copy of the notebook, are provided to the supervisor for filing with the cross-training check sheet (15.2).

Appendix H

KCEL TSS Analysis SOP

STANDARD OPERATING PROCEDURE

for

Suspended Solids - Total, 0.45 µm, and Volatile

SOP # 309v3

Date of Implementation: January 1, 2008

Supersedes SOP # 03-01-009-002

Approved by:

Author: _____ Date: _____

Supervisor: _____ Date: _____

QA Officer:_____ Date: _____

King County Environmental Laboratory
322 W. Ewing Street
Seattle WA 98119-1507

Date approved: 2/6/2008
Revision number: 3
File name: Total, Volatile and 0.45 um Suspended Solids
SOP#: 309v3

1. SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) applies to the determination of total suspended solids (TSS), volatile suspended solids (VSS) and 0.45 µm suspended solids (TSS45) in freshwater, saltwater, ground water, storm water, sewer water, domestic waste and industrial waste.

1.2 The method detection limit (MDL) is 0.5 mg/L for all three parameters (TSS, VSS and TSS45) for the analysis of 1000 mL of sample. The reporting detection limit (RDL) is 1.0 mg/L for all three parameters and all matrices except saltwater TSS, where the RDL is 10.0 mg/L. The MDL and RDL for each individual sample are automatically adjusted using actual sample volumes.

1.3 The practical range of determination is 0.5 mg/L to 40,000 mg/L. Samples are not to be diluted to extend the analytical range.

2. ASSOCIATED STANDARD OPERATING PROCEDURES

2.1 Conventionals Unit Balance Calibration SOP # 343v2.

2.2 Conventionals Unit Temperature Monitoring and Calibration Verification SOP # 342v2.

2.3 Conventionals Unit Biochemical Oxygen Demand SOP # 338v3.

3. METHOD SUMMARY

3.1 For the determination of TSS and VSS a measured volume of a well-mixed sample is filtered through a 934AH glass fiber filter. The residue retained on the glass fiber filter is dried to constant weight at 103-105°C. The resulting net weight represents the total suspended solids. For VSS the completed TSS filter is ignited at 550 ± 50°C in a muffle furnace; the resulting net weight lost represents the volatile suspended solids.

3.2 For the determination of TSS45, a measured volume of a well-mixed sample is filtered through a 0.45 µm membrane filter. The residue retained on the membrane filter is dried to constant weight at 103-105°C. The resulting net weight represents the total suspended solids, 0.45 µm.

4. INTERFERENCES

4.1 Multi-phasic samples are subject to subsampling and sample preparation errors. Difficulty with sample homogenization, volume measuring and drying to constant weight due to the presence of oil and grease in the matrix may yield questionable results.

4.2 Highly mineralized waters may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing.

4.3 Exclude large floating particles or submerged agglomerates of non-homogenous materials from the sample if it is determined that their inclusion is not representative. Excluding any material must be documented in the Solids Logbook. Samples from Industrial Waste for TSS/BOD may require blending before analysis. Follow the laboratory's BOD SOP# 03-04-007 (11.4.2).

4.4 Large amounts of residue on the filter will crust over and entrap water that will not be driven off during drying. Total residue should be limited to 200 mg. If residue exceeds 200 mg repeat the analysis using less sample. If reanalysis is not possible then check with a senior chemist or supervisor.

4.5 Prolonged filtration times resulting from filter clogging may produce biased results owing to increased colloidal materials captured on the clogged filter. The analysis should be repeated using a smaller sample volume with a new filter if filtration times exceed 10 minutes. If insufficient volume remains to obtain a quantifiable result with a new aliquot then the filtration may be completed by transferring the remaining volume to a second filtration apparatus assembled with a second pre-weighed filter. However, care should be taken to avoid this latter situation.

5. DEFINITIONS

5.1 Total Suspended Solids (TSS) – The residue retained on a glass fiber filter and dried at 103-105°C to a constant weight.

5.2 Total Suspended Solids 0.45 μm (TSS45) – The residue retained on a 0.45 μm membrane filter and dried at 103-105°C to a constant weight.

5.3 Volatile Suspended Solids (VSS) – The suspended solids lost on ignition at 550°C.

5.4 Salt Water: Samples collected from Marine Beaches and the Puget Sound with salinity over 20 PSS will be treated as Salt Water TSS samples.

5.5 The preparation date and the analysis date are defined as the day that the analysis begins.

5.6 A filtration batch is comprised of all of the samples that are grouped together and filtered at the same time on any particular day. The filtration batch may contain samples with different matrices, samples from different projects and samples in different workgroups. This allows the section the greatest flexibility for sample analysis. If the filtration batch contains samples from different matrices, then the appropriate number of matrix QC samples are filtered. If the filtration batch contains samples from different projects, then project specific QC samples are filtered. If the filtration batch contains samples from different workgroups, then the appropriate types and number of QC samples are filtered for each workgroup.

6. SAFETY

6.1 General safety- Comply with all general laboratory safety practices including: wearing a lab coat, safety glasses and gloves. Treat samples with regard to possible toxicity and microbiological potential.

6.2 Method safety

6.2.1 Use thermal protection gloves and/or long metal tongs when using the 103-105°C oven and the 550°C muffle furnace.

6.2.2 For samples not known to be hazardous, the filtrate may be discarded down the sink drain. The aluminum dishes and filters can be discarded in the garbage, after completion of the analysis and the data have been approved and moved.

6.2.3 For hazardous samples, follow the laboratory's Hazardous Waste Disposal SOP 1108v2

7. SAMPLE COLLECTION, PRESERVATION AND STORAGE

7.1 The recommended sample container is a 1 liter clear HDPE wide mouth bottle.

7.2 Samples may be stored at 4°C for 7 days.

8. APPARATUS AND EQUIPMENT

8.1 Drying oven with suitable exhaust, set at 103-105°C

8.2 Muffle furnace with suitable exhaust, set at 550 ± 50°C

8.3 Vacuum filter manifold

8.4 Filtration apparatus with coarse (40-60 µm) fritted disk or equivalent as filter support

8.5 Desiccator

8.6 Analytical balance (capable of ± 0.1 mg) – Mettler AT200

8.7 1000 mL, 500 mL, 250 mL, 100 mL, 50 mL, 25 mL, 10 mL and 5 mL graduated cylinders

8.8 Forceps and tongs

9. STANDARDS, REAGENTS AND CONSUMABLES

9.1 RO Water (ASTM Type I)

9.2 Aluminum dishes (Fisher catalog # NC9221298)

9.3 1.5 µm Glass fiber filter (Whatman 934AH, 47 mm diameter – Fisher catalog # 09-873DD)

9.4 0.45 µm membrane filter, 47mm (VWR catalog # 28147-640)

9.5 Indicating Desiccant (Fisher catalog # 07-578-3B)

9.6 Non-Indicating Desiccant (Fisher catalog # 07-577-3B)

9.7 External Laboratory Control Sample (ERA Small Lab Mineral Quality Control Sample, Catalog # 510) – A commercially prepared standard purchased through ERA. Store at 4°C. Check manufacturer's expiration date on bottle.

9.8 Working Laboratory Control Sample Diatomaceous Earth 100 mg/L: Dilute 0.2 g of diatomaceous earth (VWR catalog # JT1939-01) to 2000 mL in a two liter volumetric flask with RO water. This solution is stable for one year and is stored in a two liter HDPE bottle at 4°C. Place a label on the outside of the bottle with the chemical name, concentration, the preparation ID#, the analyst's initials, the date of preparation and the expiration date. Record all the above information in the physicals Reagent Log. Diatomaceous earth is stable under normal conditions as long as it's kept in a tightly closed container and stored at ambient temperature.

10. MAINTENANCE

10.1 Desiccator – Indicating and non-indicating desiccant mixture. Monitor indicator desiccant for moisture content. When the blue indicator desiccant turns purple, replace desiccant mixture with a fresh batch of 3 parts non-indicating and 1 part indicating desiccant.

10.2 Balance – The analyst should keep the surfaces of the analytical balance clean.

10.3 General - The counter tops should be wiped down after each use and the area should be free of clutter. The drying ovens also should be kept clean.

11. PROCEDURE

11.1 Calibration

11.1.1 Analytical balance – Refer to SOP# 343v2 Balance Calibration.

11.1.2 Drying oven – Monitor temperature daily as outlined in SOP# 342v2 Temperature Monitoring and Calibration Verification.

11.2 TSS45 Sample Preparation and Analysis

11.2.1 0.45 µm Membrane Filter Preparation

11.2.1.1 Assemble filtering apparatus by placing a 0.45 µm membrane filter (9.4) using forceps onto the filter support base attached to the vacuum manifold and placing the magnetically-sealing funnel onto the support base. Apply vacuum by turning the control valve 90° counterclockwise and rinse the filter paper with three quick rinses with the RO water spray gun. Apply vacuum until all the water has passed through. Collect the filter washings in a 20 L carboy and discard down the sink drain when the carboy is full. Carefully place the washed filters in numbered aluminum dishes placed in metal trays

and transfer the trays to the 103-105°C oven for at least one hour and no longer than 4 hours. Prepare one filter per sample plus one for each QC sample. A batch is 20 samples and it requires 1 duplicate per matrix per project, 1 method blank and 1 LCS. It is advisable to prepare extra filters for the eventuality of extremely turbid samples. Remove the trays containing the aluminum dishes and filters from the oven and store them in the desiccator for at least 1 hour. With multiple trays the cooling time in the desiccator will need to be extended beyond 1 hour.

11.2.1.2 Open the Mettler Balance Link program. The computer will automatically connect to the balance.

11.2.1.3 Open Excel and locate the **EnvLab** menu. From the **EnvLab** menu click **CNV Data Entry**. From the **Select Product(s)** menu select the appropriate template for the analysis you wish to perform and press **OK**. Enter the analysis date and the analyst's initials. Enter the dish numbers under the column labeled **Crucible #**. Save the file to the following location: I:\InstrumentData\Solids. Files are further organized into folders by month and year analyzed. Use the following naming convention for files: TSS45_YYMMDD, where YYMMDD is the year, month and day of analysis.

11.2.1.4 Remove metal tray containing the aluminum dishes and filters from the desiccator. To open or close the balance shield, press the **Select 1** or **Select 2** key. With the shield closed, tare the empty balance by pressing the **Re-Zero** key. Open the shield and place a numbered dish with a filter onto the tared balance using tongs. Do not use your hands to pick up the aluminum dishes as skin oil can add to the weight. Close the shield and weigh the dried aluminum dish with the filter. Record the weight in the Excel spreadsheet under the **Initial Crucible Weight** column next to the corresponding dish number by pressing the **Print** key. The instrument software will automatically transfer the weight displayed on the scale into the active cell on the Excel worksheet. Repeat the above steps to weigh all the dishes in order. Be sure to save the Excel file before closing it. To end the working session of the CNV Data Entry Program, click 'Exit' on the CNV Data Toolbar. The program will terminate and the toolbar will be removed from Excel. This action should be performed between weighing sessions.

11.2.2 TSS45 Sample Analysis

11.2.2.1 Assemble the filtering apparatus with the appropriate pre-weighed filters. Shake each sample well and immediately transfer to a graduated cylinder. For a method blank, filter 1000 mL of RO water. For the LCS, filter 100 mL of the diatomaceous earth 100 mg/L standard (9.8). For a laboratory duplicate, filter a maximum of half the total volume received per replicate. For non-turbid samples filter the entire volume if possible. For turbid samples, proceed in aliquots until filtration slows down but can be completed. Total filtration time should not exceed 10 minutes. If filtration time exceeds 10 minutes, assemble filtering apparatus with a new pre-weighed filter and reduce sample volume as appropriate to complete filtration. If insufficient volume remains in the sample container to pour another aliquot then the following steps may be taken. Assemble another filtering apparatus with a new pre-weighed filter and carefully transfer the remaining filtrate to it. Report the sum of the weights of the captured residues of each filter by the total volume filtered. However, care should be taken to avoid splitting an aliquot across multiple filters. Samples are not to be diluted to extend the analytical range. For turbid samples, volumes filtered can range from 5 to 500 mL. Graduated

cylinders are to be used to measure small volumes. Pipettes are not used for highly turbid samples because it's difficult to pipette a representative sample.

11.2.2.2 After filtering the sample, rinse the graduated cylinder with a small amount of RO water and pour rinsate onto the filter. Finally, rinse the filtering apparatus with three 10 mL portions of RO water with vacuum still applied.

11.2.2.3 After completing sample filtration, carefully transfer the filter into its numbered and pre weighed aluminum dish using forceps. Record the sample ID, total volume filtered and any sample observations or anomalies into the Solids Logbook. Transfer the recorded logbook information under the appropriate columns on the Excel spreadsheet file created in 11.2.1.3.

11.2.2.4 Place the metal tray containing the aluminum dishes and filters in the 103-105°C oven for at least 1 hour and no more than 4 hours. Remove the metal tray with the dishes from the oven and allow them to cool in the desiccator for at least one hour. Record the temperatures of the oven and the times in the Solids Logbook as samples are placed and removed from the oven. To reopen existing Excel spreadsheet, click 'Open File' from the CNV Data Toolbar. Using the Bal-Link program, weigh the aluminum dishes with the filter to the nearest 0.1 mg and record the weight under the **Final Crucible Weight** column of the Excel spreadsheet file created in 11.2.1.3. Press 'Calculate' on the CNV Data Toolbar to execute the calculation for TSS45. The calculation may be performed for each sample or for the entire batch. To end the working session, click 'Exit' on the CNV Data Toolbar.

11.3 TSS and VSS Sample Preparation and Analysis

11.3.1 Glass Fiber Filter Preparation

11.3.1.1 Place a glass fiber filter (9.3) with wrinkled side up onto the filtration apparatus using forceps. The filter has two distinct sides. The wrinkled side is the side without the grid crosshatches. Apply vacuum and rinse the filter with three quick rinses with the RO water spray gun. Apply vacuum until all water has passed through. Collect the filter washings in a 20 L carboy and discard down the sink drain when the carboy is full. Carefully place the washed filters into numbered aluminum dishes placed in metal trays and transfer to the appropriate oven. Prepare one filter per sample and one for each duplicate, method blank and LCS needed for the batch.

11.3.1.2 If only TSS is requested, dry the aluminum dishes with filters in the 103-105°C oven for at least one hour and no more than four hours. If both TSS and VSS are requested, dry the aluminum dishes with filters in the muffle furnace set at 550 ± 50°C for 15 minutes. Do not place metal tray in the muffle furnace. Remove the aluminum dishes with the filter from the oven and cool in the desiccator for at least 1 hour. With multiple trays the cooling time in the desiccator will need to be extended beyond 1 hour.

11.3.1.3 Open the Mettler Balance Link program. The computer will automatically connect to the balance.

11.3.1.4 Within Excel locate the EnvLab menu. From the EnvLab menu click CNV Data Entry. From the Select Product(s) menu select the appropriate template for the analysis to be performed and press OK. Enter the analysis date and the analyst's initials. Enter the dish numbers under the column labeled **Crucible #**. Save the file to I:\InstrumentData\Solids. Files are further organized into folders by year and month analyzed. Use the following naming convention for files: TSS_YYMMDD or TSSVSS_YYMMDD where YYMMDD are the year, month and date of analysis.

11.3.1.5 Remove metal tray containing the aluminum dishes and filters from the desiccator. To open or close the balance shield, press the **Select 1** or **Select 2** key. With the shield closed, tare the empty balance by pressing the **Re-Zero** key. Open the shield and place a numbered dish with a filter onto the tared balance using tongs. Do not use your hands to pick up the aluminum dishes as skin oil can add to the weight. Close the shield and weigh the dried aluminum dish with the filter. Record the weight in the Excel spreadsheet under the **Initial Crucible Weight** column next to the corresponding dish number by pressing the **Print** key. The instrument software will automatically transfer the weight displayed on the scale into the active cell on the Excel worksheet. Repeat the above steps to weigh all the dishes in order. Be sure to save the Excel file before closing it. To end the working session of the CNV Data Entry Program, click 'Exit' on the CNV Data Toolbar. The program will terminate and the toolbar will be removed from Excel. This action should be performed between weighing sessions.

11.3.2 Total Suspended and Volatile Suspended Solids Sample Analysis

11.3.2.1 Assemble the filtering apparatus with the appropriate pre-weighed filter. Shake each sample well and immediately transfer to a graduated cylinder. For a method blank, filter 1000 mL of RO water. For the Working LCS, filter 100 mL of the 100 mg/L Diatomaceous earth standard (9.8). For laboratory duplicates, filter a maximum of half the total volume received per replicate. For non-turbid samples filter the entire volume if possible. For turbid samples, proceed in aliquots until filtration slows down but can be completed. Total filtration time should not exceed 10 minutes. If filtration time exceeds 10 minutes, assemble filtering apparatus with a new pre-weighed filter and reduce sample volume as appropriate to complete filtration. If insufficient volume remains in the sample container to pour another aliquot then the following steps may be taken. Assemble another filtering apparatus with a new pre-weighed filter and carefully transfer the remaining filtrate to it. Report the sum of the weights of the captured residues of each filter by the total volume filtered. However, care should be taken to avoid splitting an aliquot across multiple filters. Samples are not to be diluted to extend the analytical range. For turbid samples, volumes filtered can range from 5 to 500 mL. Graduated cylinders are to be used to measure small volumes. Pipettes are not used for highly turbid samples because it's difficult to pipette a representative sample.

11.3.2.2 After filtering the sample, rinse the graduated cylinder with a small amount of deionized water and pour rinsate onto the filter. Finally, rinse the filtering apparatus with three 10 mL portions of RO water with vacuum still applied.

11.3.2.3 After completing sample filtration, carefully transfer the filter into its numbered and pre weighed aluminum dish using forceps. Record the sample ID, total volume filtered and any sample observations or anomalies into the Solids Logbook. Transfer the

recorded logbook information under the appropriate columns of the Excel spreadsheet file created in 11.3.1.4.

11.3.2.4 Place the metal tray containing the aluminum dishes and filters in the 103-105°C oven for at least one hour and no more than 4 hours. Remove the metal tray with the dishes from the oven and allow them to cool in the desiccator for one hour. With multiple trays the cooling time in the desiccator will need to be extended beyond 1 hour. Record the temperatures of the oven and the times in the Solids Logbook as samples are placed and removed from the oven. Typically the cycle of drying, desiccating and reweighing is not repeated because our sample residues usually dry quickly and they generally do not quickly absorb atmospheric water vapor. Reopen existing Excel spreadsheet by select 'Open File' from the CNV Data Toolbar, using the Bal-Link program, weigh the aluminum dishes with the filter to the nearest 0.1 mg and record the weight under the **Final Crucible Weight** column of the Excel spreadsheet file created in 11.3.1.4. Press 'Calculate' on the CONV Data tool bar to execute the calculation for TSS. At this point, analysis for TSS is complete. If a VSS analysis is requested, continue to step 11.3.2.5 with the completed TSS batch prepared for VSS analysis.

11.3.2.5 Using the metal tongs, carefully transfer the aluminum dishes with the filter in the muffle furnace and ignite them at 550 ± 50°C for 15 minutes. Remove the dishes from the oven, transfer them to the desiccator and allow them to cool for at least one hour. Using the Bal-Link program and Excel worksheet created in step 11.3.1.4 weigh the aluminum dishes with the filter to the nearest 0.1 mg and record the weight under the **Post-Ignition Weight** column of the Excel spreadsheet. Press 'Calculate' on the CONV Data tool bar to execute the calculation for VSS. To end the working session, click 'Exit' on the CNV Data Toolbar.

12. QA/QC REQUIREMENTS

12.1 Method QC

12.1.1 Method Blank (MB) – Method blanks are analyzed at a frequency of at least 1 in 20 samples, with at least one for each filtration batch. The absolute value of the MB should be less than MDL. If any samples are less than 10 times a detected blank, these samples may be affected. The blanks and affected samples should be redried, cooled, desiccated and reweighed. If the method blank is still out of control, check with the supervisor.

12.1.2 Laboratory Control Samples (LCS):

12.1.2.1 At least one LCS (9.8) is analyzed with every batch for TSS and TSS45. The LCS should be within 20% of the true value (100 mg/L). If the LCS is out of control, check first for dish ID mix-up. If the sample and the dish ID are not the source, dry, cool and reweigh the LCS. If the LCS is still out of control, check with supervisor.

12.1.2.2 An LCS is not analyzed for VSS because one is not available.

12.1.3 External Laboratory Control Samples (9.7) are QC samples with certified values from an external source. One External LCS is analyzed with each new preparation batch of the in-house LCS (9.8). The External LCS is used to verify the performance of the new batch.

External LCS is also analyzed in conjunction with all Performance Evaluation (PE) samples. The external LCS must meet performance windows from the vendor.

12.2 Matrix QC

12.2.1 Laboratory Duplicates (LD) – Laboratory duplicates are analyzed at a frequency of 1 duplicate per 20 samples, per matrix, per project. Analyze at least one duplicate for each filtration batch unless insufficient sample volumes are available. The absolute value of the relative percent difference (RPD) should be ≤ 25% for values ≥ RDL. If the RPD exceeds the control limit, check first for an aluminum dish/sample ID mixup. If sample and dish identification are not the source, dry, cool and reweigh the sample and LD. If the RPD is still out of control, repeat analysis if sample volume is available and holding time can be met. If problem is not resolved, check with supervisor. If the reported RPD exceeds the control limit, fill out a data anomaly form to document the problem, probable cause, corrective action and impact on data.

12.2.2 Matrix Spikes (MS) – Matrix spikes are not analyzed for this parameter.

12.3 Corrective Actions: Any action taken that corrects a QC failure should typically be applied to all samples in the batch unless it is clear that the problem was isolated to the QC sample itself.

12.4 MDL Studies and Validation Procedures – A minimum of a one day method detection limit study is performed yearly to verify the existing detection limits, alternating TSS one year and TSS45 the next. A three day (non-consecutive) MDL study may be required to re-establish an appropriate MDL following major methodology modifications. Each day of a MDL study consists of analyzing at least seven replicates of a standard at or near the reporting detection limit of each analyte. See the Quality Assurance Manual Appendix E, section B for details on MDL determination. Hardcopies of the calculated MDLs and raw data are maintained in the conventionals lab within the "MDL Studies" cabinet. See section Appendix H of the Quality Assurance Manual for further detail on method validation criteria.

13. DATA REDUCTION, REPORTING AND DOCUMENTATION

13.1 Calculations – All formulas used in calculations are maintained in protected VBA modules within an Excel spreadsheet to eliminate accidental manipulation.

13.1.1 Calculations for Total Suspended Solids 45 µm (TSS45),

$$mg / L = \frac{(A - B) \cdot 10^6}{V}$$

Where:

A = weight of the dried residue + aluminum dish and filter (Final Crucible Weight) in g.
B = weight of dried aluminum dish and filter (Initial Crucible Weight) in g.
V = volume of sample, mL.

13.1.2 Calculations for Total Suspended Solids (TSS),

$$mg/L = \frac{(A-B)\cdot 10^6}{V}$$

Where:

A = weight of the dried residue + aluminum dish and filter (Final Crucible Weight) in g.
B = weight of dried aluminum dish and filter (Initial Crucible Weight) in g.
V = volume of sample, mL.

13.1.3 Calculations for Volatile Suspended Solids (VSS),

$$mg/L = \frac{(A-B)\cdot 10^6}{V}$$

Where:

A = weight of the dried residue + aluminum dish and filter before ignition (Final Crucible Weight) in g.
B = weight of the residue + aluminum dish and filter after ignition (Post-Ignition Weight) in g.
V = volume of sample, mL

13.1.4 Calculations for Method Detection Limits (MDLs), mg/L = 1000/V *0.5

$$mg/L = \frac{1000}{V}\cdot 0.5$$

Where:

V = volume of sample, mL

13.1.5 Calculations for Reporting Detection Limits (RDLs) for all samples except saltwater TSS,

$$mg/L = \frac{1000}{V}\cdot 1.0$$

Where:

V = volume of sample, mL

13.1.6 Calculations for Reporting Detection Limits (RDLs) for saltwater TSS,

$$mg/L = \frac{1000}{V}\cdot 10.0$$

Where:

V = volume of sample, mL

13.2 Reporting

13.2.1 Workgrouping in LIMS **-** Prior to data entry to the LIMS, all samples and associated QC must be assigned a unique workgroup number in LIMS. The following procedures apply to generating a workgroup:

13.2.1.1 Within LIMS select "Sample Management" followed by "Workstat" to reach the "Workgroup Management" form.

13.2.1.2 Select the "New" command button and, at a minimum, enter a description for the workgroup in the "Description" field and enter your initials in the "Operator" field. Note that the "Prep Date" field should be left blank. Conventionals preparation date data must be entered via the CSV file during data entry.

13.2.1.3 Select the "OK" command button once completed to return to the "Workgroup Management" form. At a minimum, the "Department", "Status" and "Product" fields must be entered to query data for association to the newly created workgroup. Additional information including matrix, login numbers, sample numbers, etc., also can be entered to assist the query.

13.2.1.3.1 The "Department" must be entered as the number 3 which indicates the conventionals laboratory unit.

13.2.1.3.2 The "Product" code used must be an existing LIMS product name; i.e., TSS, TSS45 or VSS.

13.2.1.3.3 The "Status" field should be updated from "NEED" to "WKGP", "PREP" or "ANAL" to identify the samples as workgrouped, prepared or analyzed respectively. The status code used is at the discretion of the analyst; however, the code used should reflect the current conditions of the associated samples. The status of a workgroup should be updated as changes are made (i.e., updated from "PREP" to "ANAL" once analysis has been completed).

13.2.1.4 Once all the necessary query information has been entered, select the "OK" button at the bottom of the "Workgroup Management" form. On the "Work Group / Status Editor" form that appears, select the samples to be added to the workgroup by placing an "X" in the far left field. Once completed select the "Save" command button at the bottom of the screen then "Cancel" to return to the "Workgroup Management" form.

13.2.1.5 To enter associated QC, select the "ADD QC" command button at the bottom of the "Workgroup Management" form. On the "QC Samples" form that appears, the following information must be added for each QC sample in the workgroup.

13.2.1.5.1 Matrix – two character LIMS matrix code (e.g., LN, LE, LK). Method QC including MBs and LCSs, must be entered with the matrix code "LN" to identify these as blank waters. Matrix QC including LDs must be entered with the matrix code of the associated samples to which they are linked.

13.2.1.5.2 Product - LIMS product name that must match the product(s) of the associated samples in the workgroup; i.e., TSS, TSS45 or VSS.

13.2.1.5.3 QC Type – LIMS code identifying the QC type associated with the specific sample. Applicable QC type codes for suspended solids analysis include MB, LCS and LD.

13.2.1.5.4 Reference – This field is used to reference associated sample IDs or look-up table references such that QC calculations can be performed automatically by the LIMS QC module. The following general rules apply to assigning references to QC samples:

13.2.1.5.4.1 MB – No look-up table is available and therefore no unique entry is required. In general, the sample ID used for the method blank is entered so that multiple method blanks in a workgroup can be differentiated by their reference on the workgroup report (i.e., MB1 050402 to identify the first method blank from April 2, 2005).

13.2.1.5.4.2 LCS – Each lab control sample must reference the correct List Function ID from the associated look-up table. The established suspended solids List Function is LEVEL1.

13.2.1.5.4.3 LD – Each lab duplicate must reference the LIMS sample number to which it is associated (i.e., L12345-1).

13.2.1.6 Once completed select the "Save" command button at the bottom of the screen then "Cancel" to return to the "Workgroup Management" form. The workgroup creation is completed and the workgroup is now ready for data entry.

13.3 LIMS Data Entry – Data to be sent to the LIMS can be prepared by using certified macros (Section 13.4) or can be prepared manually.

13.3.1 For manual preparation, open the original file (*.xls) in Excel. Format the data into appropriate columns and convert it to a *.csv file as shown below in Section 13.3.2. Save this file to the directory "\\dnrlab-spud\s3cvxl" which is designated as the "G" drive.

13.3.2 Data is submitted to LIMS as a comma separated variable format and is created in the format displayed below. The file contains the listed elements in the designated location to correctly transfer to the LIMS. The MDL and RDL information does not have to be included for the data to be sent, but allows the MDL and RDL values to be easily changed based upon required dilutions.

WG12345 Sample Number Date Analyzed	CVTSS mg/L 6/23/2005	Prep Date	MDL	RDL
WG12345-1	0.0000	6/23/2005	0.5	1
WG12345-2	95.0000	6/23/2005	5	10
L12345-1	0.4000	6/23/2005	0.5	1
L12345-2	3.8000	6/23/2005	0.5	1
L12345-3	7.8000	6/23/2005	1	2

13.3.2.1 Workgroup Number - LIMS derived identification which defines one batch of analytical data and all associated QC.

13.3.2.2 Sample Number - LIMS derived identification that is unique to a given sample. Includes LIMS derived QC sample numbers (i.e., WG12345-1) used for the reporting of QC associated with a given workgroup.

13.3.2.3 Date Analyzed - Date on which the oven drying was initiated. Only one date analyzed is specified per CSV file. Samples analyzed on different dates but included in the same workgroup must be sent to LIMS on separate CSV files.

13.3.2.4 Prep Date - The Prep Date and Date Analyzed are the same for suspended solids products.

13.3.2.5 Units - Analytical units associated with the reported data. Units are defined as mg/L.

13.3.2.6 List Type - The specific parameter name associated with a particular product analyzed. The listtype CVTSS is used for total suspended solids, CVTSS45 for total suspended solids, 0.45 µm and CVVSS for volatile suspended solids.

13.3.2.7 MDL - Method detection limits entered on a sample by sample basis. Addition of this element to the CSV file is optional. If no adjustments are required to the default LIMS limits, MDLs do not need to be loaded to LIMS through the CSV file.

13.3.2.8 RDL - Reporting detection limits entered on a sample by sample basis. Addition of this element to the CSV file is optional. If no adjustments are required to the default LIMS limits, RDLs do not need to be loaded to LIMS through the CSV file.

13.4 Data Reduction Tools **-** Certified Excel macros, using Visual Basic for Applications (VBA), are utilized for assisting in the data reduction process. The macros available provide an automated means of report formatting and CSV file creation that are consistent between analysts. The following procedures apply to formatting result files and generating CSV files in the necessary format to be loaded to the LIMS.

13.4.1 Activate the solids data entry tool by selecting CNV Data Entry from the EnvLab menu.

13.4.2 Select Open existing file and click OK. Choose the suspended solids data file (*.xls) created in Section 11.2.1.3 or 11.3.1.4 and click Open.

13.4.3 Enter workgroup information pertaining to assigned QC identifiers in LIMS and print this sheet for the final data package.

13.4.4 Select Create CSV and create the CSV file to be sent to LIMS.

13.4.4.1 After formatting has been done by the macro, look for any corrections that may need to be made for the sheet before continuing. Most common corrections may have to be made based upon errors in entering sample numbers or failing to assign a WG-# identifier to QC.

13.4.5 The final CSV file should be sent to LIMS using the internal Laboratory data loading tool.

13.4.5.1 Select the EnvLab button in the toolbar, followed by the CNV Data Entry button. Click on Load LIMS. This will send data to LIMS and at the same time will confirm that the CSV file has data which matches the assigned LIMS sample identification. This also stores data for comparison purposes as needed.

13.5 LIMS Association of Sample and QC – By default, all samples in a given workgroup are associated by LIMS to all QC samples included in the workgroup. This potentially results in an over association of samples to QC in LIMS. The only qualifier applicable to conventionals that could be applied automatically by LIMS is the "B" qualifier which indicates blank contamination. Therefore, the analyst is responsible for reviewing all occurrences of LIMS qualified "B" data and confirming appropriateness. A sample should only receive B qualification if it was a member of a filtration batch containing a failed method blank. A sample receiving B qualification that was not a member of the filtration batch containing a failed method blank should not be qualified. In cases where samples have received qualification where it is not appropriate, the analyst must manually remove the qualifier from the data. See section 13.2.1.5 for further details on sample and method blank associations.

13.6 Data Package **-** The data package shall include the workgroup review sheet, workgroup report, LIMS chain report, instrument charts, the data file, photocopies of analysis and logbook pages, photocopy of the preparation logbook, CSV files and LIMS QC report. A data anomaly form must be included in the event that any data were qualified. In addition, a sample receipt record (from sample login) must also be included for instances where anomalies were observed upon sample receipt at the laboratory and corrective action steps taken prior to sample analysis.

13.6.1 Within Excel open the CNV Data Entry Program – see 11.2.1.3, select 'Open File' from CNV Data Toolbar to open the Excel spreadsheet created in 11.2.1.3 or 11.3.1.4. To create a CSV file for export to LIMS select 'Create CSV' from the CNV Data Toolbar. Once selected, a new worksheet is created within the same workbook that contains the CSV file automatically. Verify that all the data and sample IDs are correct and save the excel workbook under folder in I:\InstrumentData\solids\YYMM.

13.6.2 While on the CSV portion of the excel workbook press 'Load LIMS' on the CNV Data Toolbar to post data to LIMS. If Multiple CSV files are present, this action must be

performed for each individual CSV file. The LIMS calculation will apply significant figure logic and qualify data based on matrix, QC results and sample concentrations. To end the working session of the CNV Data Entry Program, click 'Exit' on the CNV Data Toolbar.

13.7 Documentation

13.7.1 Solids Logbook – Each page should contain the parameter, date analyzed, analyst's initials, sample #, crucible #, sample volumes, times, temperatures of the oven and comments. In the comments section, record any unusual sample observations and anomalies and the workgroup information.

13.7.2 Excel XLS Spreadsheet File – The Excel file will contain the initial crucible weight in grams, the final crucible weight in grams, total suspended solids in mg/L and volatile suspended solids in mg/L (if applicable) in addition to the corresponding lab notebook information.

14. REFERENCES

14.1 Method 2540D & E, *Standard Methods for the Examination of Water and Wastewater*, 20th. ed, 1998, pp. 2-57 and 2-58.

14.2 Residue, Non-Filterable (Gravimetric dried at 103-105°C), EPA Method 160.2, (1983).

14.3 Residue, Volatile (Gravimetric ignited at 550°C), EPA Method 160.4, (1983).

14.4 King County Environmental Laboratory QA Manual, (2006).

15. TRAINING OUTLINE

15.1 The steps followed for training a new analyst is to demonstrate the preparation and analysis of TSS, TVS and TSS45, explaining each step of the procedure and using the SOP as an aid. The analyst-in-training then prepares samples, performs routine maintenance on the instrument and analyzes samples while being observed by the trainer, who answers questions, provides feedback on technique and further explains the steps in the procedure. The trainer continues to observe the analyst-in-training on a daily basis until both are comfortable that the new analyst is competent to perform the procedure.

15.2 All training is documented using the Conventional Section Cross-Training Guidelines Check Sheet. This sheet outlines the major issues that must be addressed in order to complete the training. This sheet documents who was involved in the training and when specific aspects of the training were completed. The completed check sheet is maintained on file by the supervisor.

15.3 In order to complete the training, the trainee must analyze a set of blind samples prepared by the trainer. Upon successful analysis of the blind samples, a complete data package including instrument report and a copy of the notebook, are provided to the supervisor. These are filed along with the cross-training check sheet.